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Jennifer Guerra

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicants: Yuichi Mori, et al.

Serial No.: 10/647,076

Filed   : August 22, 2003

For   : PLANT CULTIVATING CONTAINER AND PLANT CULTIVATING
            METHOD

Art Unit : 3643

Examiner : Jeffrey L. Gellner

DECLARATION UNDER 37 C.F.R. 1.132

    I, Hiroshi Yoshioka, a Japanese citizen residing at Shimo-
Ochiai 11-1, Hadano-shi, Kanagawa-ken, Japan, declare and say:

    I took a master course majoring in applied chemistry at the
Graduate School of Science and Engineering, Waseda University and I
was graduated therefrom in March 1984.

    In 1984, I entered Terumo Corporation, Japan.

    In 1990, I entered W.R. Grace & Co. (Central Research Labora-
tories in Japan).

    In 1995, I obtained a doctorate in engineering from Waseda
University. In that year, I entered Mebiol Inc. Since then, I have
been engaged in fundamental studies, research and development of
polymer materials used in the medical and agricultural fields.

    I am the Executive Vice President of Mebiol Inc.

    I am also a visiting associate professor of Advanced Research
Institute for Science & Engineering of Waseda University and a

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part-time lecturer at St. Marianna University School of Medicine.

I am well familiar with the present case.

I have read and understood the Office Action dated November 20, 2007 and references cited therein.

I have conducted experiments and observations to evaluate the plant growth using a non-porous PVA film recited in claim 1 of the present application and various films described in **Weder et al.** (USP 5,363,592) and **Sakai** (JP7-45169). The materials, methods and results are described in a paper attached hereto and marked "Exhibit 1".

From the results of Exhibit 1, it can be fairly concluded:

(1)   that the system of the present invention is advantageous in that, simply by supplying water in the water tank to a plant through such a non-porous PVA film, the rhizosphere environment (such as humidity and oxygen concentration) can be easily and favorably maintained for a long time even without directly supplying water to the culture soil disposed on the film, thereby enabling very rapid and full growth of a plant with less amount of water (Experiment 1A shown in Table A of Exhibit 1, Experiment 1 of the 1st Okamoto Declaration (filed on January 20, 2004) shown in Table B of Exhibit 1, and Experiment 3 of the 2nd Okamoto Declaration (filed on August 15, 2005) shown in Table B of Exhibit 1),

(2) that, on the other hand, a porous hydrophobic film (such as a polypropylene film described in **Weder** et al. and a PTFE film described in **Sakai**) cannot transmit therethrough a sufficient amount of moisture (Comparative Experiment 1A shown in

Table A of Exhibit 1, and Experiment 1 of the 1st Okamoto Declaration shown in Table B of Exhibit 1) and is likely to lose its impermeability to liquid water during the cultivation of a plant, so that a porous hydrophobic film cannot be used for maintaining favorable rhizosphere environment (such as moisture and oxygen content) for a long time (Experiment 1 of the 1st Okamoto Declaration shown in Table B of Exhibit 1),

(3) that, even if a microporous hydrophobic film is hydrophilized, the resultant film freely passes water therethrough so that such a hydrophilized film cannot be used for controlling the rhizosphere environment of a plant (Experiment 2 of the 1st Okamoto Declaration shown in Table B of Exhibit 1),

(4) that, further, the water vapor permselective films, such as a silicone film, a polyimide film and a cellulose acetate film, which are described in **Sakai** cannot supply sufficient amount of water to the plant through the film (Comparative Experiments 2A and 3A shown in Table A of Exhibit 1) so that the plant growth using any of such films is poor,

(5) that, furthermore, a cellophane film described in **Weder** et al. is broken when used in a manner as in the system of the present invention (Experiment 2 of the 2nd Okamoto Declaration shown in Table B of Exhibit 1),

(6) that, from items (1) to (5) above, it is apparent that the use of non-porous PVA film is essential for achieving the above-mentioned excellent effects of the system of the present invention.

The undersigned petitioner declares that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: May 20, 2009
_____

_____
Hiroshi Yoshioka

EXHIBIT 1

Exhibit 1

Experiments and observations to evaluate the plant growth using the non-porous polyvinyl alcohol film recited in claim 1 of the present application and various films described in **Weder et al.** (USP 5,363,592) and **Sakai** (JP7-45169)

I.   Object of the experiments:

The Examiner recognizes that neither **Weder et al.** (USP 5,363,592) nor **Sakai** (JP7-45169) describes the use of the non-porous polyvinyl alcohol (PVA) film recited in claim 1 of the present application; however, the Examiner takes a position that **Weder et al.** and **Sakai** describe the use of a cellulose film (which may be a non-porous hydrophilic film as in the case of a non-porous PVA film) and, hence, it is obvious for those skilled in the art to replace the cellulose film described in **Weder et al.** and **Sakai** by "a longer lasting material", such as a PVA film which has been known from **Schur** (USP 3,097,787) and **Caldwell** (USP 2,773,050).

However, it should be noted that, as can be seen from claim 1 of the present application (amended on March 11, 2009), the plant-cultivating system of the present invention is characterized in that a non-porous PVA film is provided in a water tank such that cultivation of a plant can be performed while supplying water to a plant through the non-porous PVA film. In the present invention, simply by supplying water in the water tank to a plant through such a non-porous PVA film, the

rhizosphere environment (such as humidity and oxygen concentration) can be easily and favorably maintained for a long time even without directly supplying water to the culture soil disposed on the film, thereby enabling very rapid and full growth of a plant with less amount of water (see page 1, lines 13 to 19 of the present specification and the Working Examples of the present application).

On the other hand, **Weder et al.** describe the use of "a polypropylene film" and "a cellophane" (col. 2, lines 50 to 52) as a "liner" used in a container for a propagule and a growing medium, and **Sakai** describes the use of "a silicone film, a cellulose acetate film (cellulose-type film) and a polyimide film" (col. 5, lines 9 to 16) as a water vapor perm-selective film which may be combined with a waterproof mois-ture-permeable film, such a porous polytetrafluoroethylene film. However, by the use of such films as described in these references, the rhizosphere environment cannot be favorably controlled for a long time. In addition, neither **Weder et al.** nor **Sakai** has any teaching or suggestion about the control of the rhizosphere environment (such as humidity and oxygen con-centration) by supplying water to a plant through such films as described in these references to the plant.

Further, **Schur** and **Caldwell** describe a PVA film but have no teaching or suggestion that any advantage will be obtained by using a non-porous PVA film for cultivation of a plant. In addition, **Sakai** rather teaches away from the use of a non-porous PVA film.

Thus, the excellent effects achieved by the use of a non-porous PVA film are <u>neither</u> taught nor suggested by any of the cited references including **Schur** and **Caldwell** and, hence, are <u>unexpected</u> and <u>surprising</u>.

For substantiating this, observations and experiments are conducted as follows.

II. Methods and Materials:

II-1) Observations on the cited prior art references

II-1-i) Disclosure of Weder et al.

Weder et al. describe "a polypropylene film" and "a cellophane" as "polymer film" usable as "liner 28" shown in Figs. 1, 2, 3, etc. of **Weder et al.** (col. 2, lines 50 to 52).

However, <u>nowhere</u> in **Weder et al.** can be found any teaching or suggestion about cultivation of a plant by proving water through the film used as liner 28. That is, "liner 28" is used only as a liner, and the "growing medium 40" (such as water and culture soil) and "botanical item 42" are provided only in liner 28 as shown in Fig. 1 of **Weder et al.** For this reason, **Weder et al.** have <u>no</u> description about whether or not the film used as liner 28 is porous and have <u>no</u> description about the permeability of the film to water or water vapor.

Needless to say, since polypropylene is hydrophobic, if the polypropylene film mentioned in **Weder et al.** is non-porous, the film exhibits substantially <u>no</u> permeability to water or water vapor, so that such a film can<u>not</u> be used for cultivat-

ing a plant in such a manner as in the present invention.

Therefore, in Comparative Experiment 1A below, a commercially available microporous polypropylene film having a moisture vapor permeability was used (despite that **Weder et al**. do not describe that the polypropylene film is porous) since an experiment using a non-porous hydrophobic film is meaningless.

Further, it should be noted that, in Mr. Okamoto Declaration filed on January 20, 2004 (hereinafter, referred to as "1st Okamoto Declaration"), plant cultivation was performed for a longer period of time than in Comparative Experiment 1A, using the same microporous polypropylene film as used in Comparative Experiment 1A, and a hydrophilized microporous polypropylene film obtained by subjecting the microporous polypropylene to hydrophilicity-imparting treatment. On this point, observation will be made later in item II-3) below.

With respect to the cellophane (cellulose) film mentioned in **Weder et al**., in Mr. Okamoto Declaration filed on August 15, 2005 (hereinafter, referred to as "2nd Okamoto Declaration"), plant cultivation was performed using a non-porous hydrophilic cellophane film. Also on this point, observation will be made later in item II-3) below.

II-1-ii) Disclosure of **Sakai**

Since the Derwent English translation of **Sakai** on which the Examiner relies is not so good, a verified partial English translation of **Sakai** which contains better English translations is submitted herewith as Attachment 1.

Those skilled in the art would not consider that any advantage will be obtained by application of a non-porous PVA film to **Sakai**. and, rather, considers that the use of a non-porous PVA film is not suitable for the object of **Sakai**. The reason for this is as follows.

The object of **Sakai** is to provide "a plant cultivating apparatus for use in lands and water areas unsuitable for cultivating plants, wherein said apparatus is capable of supplying water for cultivating and growing plants while effectively preventing adverse effects of harmful moisture present in the land or water area and of harmful gases generated from the harmful moisture" (see page 2, lines 1 to 8 of Attachment 1).

Therefore, in **Sakai**, it is most important to remove harmful substances including harmful gases which are contained in or generated from the seawater, waste water, etc. On the other hand, in **Sakai**, the moisture of the rhizosphere is controlled rather by supplying water from above the plant at least after the growth of a plant has reached a certain stage. This is apparent from the following description of Sakai:

> "Further, vinyl sheet 8 will guide water from rain-falls and the like to the periphery of plant 9 and feed the water to culture soil 7.
> It is apparent that the present utility model can be used as a preferred means for supplying water needed for plant growth. However, it is also apparent that water requirement of a plant will increase in accordance with the plant growth and increasing plant size. When the water requirement increases, the present utility model can be used as a means for water saving. In this case, it is consequential to
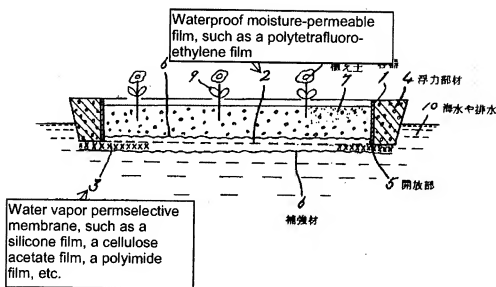
use the present utility model <u>in combination with</u>
<u>the above-mentioned conventional methods for supply-</u>
<u>ing water or methods for water saving</u>." (emphasis
added)(item 5 of Attachment 1)

For removal of non-volatile harmful substances and harm-

ful gases, **Sakai** uses a waterproof moisture-permeable film,

such as a porous polytetrafluoroethylene (PTFE). It is well

known in the art that a porous PTFE film generally has a poor

gas barrier property which, however, may vary to same extent

depending on the pore structure (such as porosity and pore di-

ameter) thereof. This is apparent from the fact that **Sakai**

describes the use of a PTFE film having a "Gurley number of

from 0.1 to 100 seconds" (see item 4 of Attachment 1). There-

fore, when the gas barrier property of the PTFE film (water-

proof moisture-permeable film) is not sufficiently high, **Sakai**

uses a water vapor permselective membrane (such as a silicone

film, a cellulose acetate film, or a polyimide film) to pre-

vent the intrusion of harmful gas into the culture soil, as

apparent from the following description of **Sakai**:

"As explained above, when <u>methane gas and other</u>
<u>gases</u> which are harmful to plants are present in
drainage or the like, the <u>water vapor permselective</u>
<u>membrane</u> is used to prevent the entry of such harm-
ful components into the culture soil disposed inside
framework 1." (emphasis added)(see item 3 of Attach-
ment 1)

Thus, when the PTFE film 2 cannot sufficiently prevent trans-

mission of harmful gas therethrough, water vapor permselective

film 3 (such as "a silicone film, a cellulose acetate film (cellulose-type film) and a polyimide film") having a high gas barrier property is laminated on the PTFE film. For easy understanding of the device of **Sakai**, Fig. 1 of **Sakai** is reproduced below, to which explanations on the films have been added.

Waterproof moisture-permeable film, such as a polytetrafluoro-ethylene film

Water vapor permselective membrane, such as a silicone film, a cellulose acetate film, a polyimide film, etc.

浮力部材
海水や排水
開放部
補強材

In this connection, it should be noted that a non-porous PVA film has a gas barrier property; however, it is well known in the art that the gas barrier property of a non-porous PVA film is <u>drastically lowered</u> under <u>high humidity</u> conditions. For example, reference is made to Polymer Handbook, Fourth Edition, Volume 2, "Permeability and Diffusion Data", pp.543-568, Wiley-Interscience, A John Wiley & Sons, Inc, Publication, 1999 (submitted herewith as Attachment 2); V. L. Simril and A.

Hershberger, Modern Plastics, pp. 95-102, July, 1950 (submitted herewith Attachment 3); and Polymer Chemistry, Vol.19, 191, pp. 158-162, 1961 (submitted herewith as Attachment 4). Attachments 2 and 3 teach that, at 24 to 25 °C, the gas barrier property of a PVA film measured at a relative humidity of 100 % is less than 1/7,000 of that measured at a relative humidity of 0 %. Attachment 3 teaches that, at 23 °C, the gas barrier property of a PVA film measured at a relative humidity of 94 % is about 1/12,000 of that measured at a relative humidity of 0 %. Further, Attachment 4 also teaches that the gas barrier property of a cellulose acetate film as described in **Sakai** is not influenced by the humidity and is higher than that of a PVA film at a high humidity.

Thus, it is apparent that those skilled in the art would not replace the films described in **Sakai** with a non-porous PVA film which exhibits very poor gas barrier property at a high humidity, in view of the fact that the system of **Sakai** is necessarily used under high humidity conditions and the film used in **Sakai** needs to exhibit a high gas barrier property under high humidity conditions.

With respect to porous PTFE film 2 used in **Sakai**, porous PTFE film 2 may maintain its selective permeability to water vapor for a while during the use of the system of **Sakai**. However, as well known in the art, unless the quality of water is strictly controlled, the surface tension of the water generally lowers due to the presence of impurities. Therefore, after a while, the porous PTFE film 2 becomes permeable to liq-

uid water and loses the control over the water transmission therethrough. This is apparent from Experiment 2 of the 1st Okamoto Declaration where a microporous polypropylene film (i.e., a microporous hydrophobic film as in the case of the PTFE film used in **Sakai**) having a small average porous diameter became permeable to water 2 months after the start of the cultivation. On this point, more detailed explanation is made in item II-3) below.

On the other hand, the present invention has been made based on a surprising finding that, simply by supplying water in the water tank to a plant through such a non-porous PVA film, the rhizosphere environment (such as humidity and oxygen concentration) can be easily and favorably maintained for a long time even without directly supplying water to the culture soil disposed on the film, thereby enabling very rapid and full growth of a plant with less amount of water.

By the use of films as described in **Sakai**, such excellent effects cannot be obtained.

In order to substantiate this, plant cultivation was performed using commercially available, water vapor permselective films made of silicone and polyimide in Comparative Experiments 2A and 3A described below, respectively.

With respect to "a cellulose acetate film" mentioned in **Sakai** as a water vapor permselective film, a commercially available product could not be found. Therefore, plant cultivation was performed in Comparative Experiment 4A below using a non-commercially available cellulose acetate film (which is

water vapor permselective) directly obtained from Konica Mi-
nolta Opto, Inc., Japan. On this point, it should be noted
that cellulose acetate is an acetyl ester of cellulose and,
therefore, is totally different from cellulose per se in prop-
erties such as hydrophilicity.

With respect to the films used in Comparative Experiments
2A, 3A and 4A, each of the films is a non-porous water vapor
permselective film, and has almost the highest water vapor-
permeability among the known non-porous films (made of sili-
cone, polyimide or cellulose acetate).

II-2) Experiment and Comparative Experiments

Experiment 1A (Present invention):

Preparation of Plant-cultivating System

A plant-cultivating system was prepared as follows. A
resin container (inner length: 20 cm, inner width: 12 cm,
depth: 5.5 cm) was installed on the ground and filled with 700
ml of a tap water. A non-porous polyvinyl alcohol (PVA) film
(thickness: 40 μm, manufactured and sold by Aicello Chemical
Co., Ltd.) having a size of 30 cm × 22 cm was used as a non-
porous hydrophilic film. On the film was placed about 170 g
of commercially available soil (tradename: Super-mix A, sold
by Sakata Seed Co., Ltd., Japan), thereby obtaining the plant-
cultivating system of the present invention.

With respect to the non-porous PVA film, the moisture va-
por-permeability thereof was 2,200 $g/m^2 \cdot 24$ hours as measured in

accordance with JIS K 7129.

Cultivation of Plants

Using the prepared plant-cultivating system, cultivation
of seedlings of arugula (Binomial name: *Eruca sativa* (also
known as "rocket" or "rucola")) was performed in the following
manner.

Total of six arugula seedlings (tradename: "Odessey",
sold by Sakata Seed Co., Ltd., Japan) were planted in the cul-
ture soil disposed on the non-porous PVA film. The planting
of the seedlings was performed on the 17th day after the dis-
semination, and each of the seedlings at the time of the
planting had one foliage leaf. The planted seedlings were
cultivated in a cultivation rack at a temperature of 21 °C and
a relative humidity of 60 to 70 %, while exposing the seedling
to an artificial illumination having an intensity of 3,700 to
3,800 lux, during the period of from February 23, 2009 to
April 2, 2009.

Evaluation of cultivated plants

The cultivated six arugula plants (namely the leaves and
the stems of the plants) were harvested on day 39 from the
start of the cultivation. With respect to the six plants, the
heights were measured, and the number of leaves was counted to
obtain an average number of leaves of the six plants.

Comparative Experiment 1A (using a non-treated microporous

polypropylene film)

A plant-cultivating system was prepared in substantially the same manner as in Experiment 1A above except that a microporous polypropylene film (thickness : 40 μm) (PH-35 manufactured and sold by Tokuyama Corp., Japan) was used instead of the non-porous PVA film.

With respect to the microporous polypropylene film, the moisture vapor-permeability thereof was 734 g/m^2·24 hours as measured in accordance with JIS K 7129.

Using the prepared plant-cultivating system, cultivation of seedlings of arugula was performed in the same manner as in Experiment 1A, and the results of the cultivation were evaluated in the same manner as in Experiment 1A.

Comparative Experiment 2A (using a silicone film)

A plant-cultivating system was prepared in substantially the same manner as in Experiment 1A above except that a silicone film (thickness : 40 μm) (tradename: "Keiju", manufactured and sold by Mitsubishi Plastics Inc., Japan) was used instead of the non-porous PVA film.

With respect to the silicone film, the moisture vapor-permeability thereof was 100 g/m^2·24 hours as measured in accordance with JIS K 7129.

Using the prepared plant-cultivating system, cultivation of seedlings of arugula was performed in the same manner as in Experiment 1A, and the results of the cultivation were evaluated in the same manner as in Experiment 1A.

Comparative Experiment 3A (using a polyimide film)

A plant-cultivating system was prepared in substantially the same manner as in Experiment 1A above except that a polyimide film (thickness : 40 μm) (tradename: "Kapton", manufactured and sold by Du Pont-Toray Co., Ltd., Japan) was used instead of the non-porous PVA film.

With respect to the polyimide film, the moisture vapor-permeability thereof was 84 $g/m^2 \cdot 24$ hours as measured in accordance with JIS K 7129.

Using the prepared plant-cultivating system, cultivation of seedlings of arugula was performed in the same manner as in Experiment 1A, and the results of the cultivation were evaluated in the same manner as in Experiment 1A.

Comparative Experiment 4A (using a cellulose acetate film)

A plant-cultivating system was prepared in substantially the same manner as in Experiment 1A above except that a cellulose acetate film (thickness : 40 μm) (obtained from Konica Minolta Opto, Inc., Japan) was used instead of the non-porous PVA film.

With respect to the cellulose acetate film, the moisture vapor-permeability thereof was 710 $g/m^2 \cdot 24$ hours as measured in accordance with JIS K 7129.

Using the prepared plant-cultivating system, cultivation of seedlings of arugula was performed in the same manner as in Experiment 1A, and the results of the cultivation were evalu-

ated in the same manner as in Experiment 1A.

    II-3) Observations based on the 1st Okamoto Declaration
filed on January 20, 2004 and the 2nd Okamoto Declaration
filed on August 15, 2005

1st Okamoto Declaration

    In the 1st Okamoto Declaration, cultivation of plants was
performed using a non-porous PVA film (Experiments 1 and 2)
and two types of microporous polypropylene films, i.e., a mi-
croporous polypropylene film (Experiment 1) which inherently
is hydrophobic, and a hydrophilized microporous polypropylene
film (Experiment 2), which are hereinafter referred to as
"non-treated microporous PP film" and "hydrophilized micropor-
ous PP film", respectively.

    The results of the cultivation in Experiment 1 were as
follows:

    "As a result of the cultivation, the above pansy
    seedlings were smoothly grown for about 2 months
    without directly supplying additional water to the
    soil. However, immediately thereafter, only the
    soil surrounded by the microporous polypropylene
    film began to be wetted, and after a while, the soil
    was immersed in water. When the microporous film
    was carefully observed, but there was no holes or
    cracks such as breakage in the film.

    On the other hand, with respect to the PVA film-
    covered container, the pansy seedlings were smoothly
    grown for 3 months or more." (emphasis added)(page 4,
    2nd and 3rd para. of the 1st Okamoto Declaration)

As apparent from the above, the non-treated microporous PP film functioned for the first 2 months as "water vapor permselective film" which "selectively allows water vapor to permeate therethrough" as recited in **Sakai**; however, after that period, liquid water **freely passed through** the micropores of the film. This phenomenon is considered to be caused by lowering of the surface tension of the water due to the intrusion of impurities into water. In this connection, it should be noted that, in Experiment 1 of the 1st Okamoto Declaration, "After a few weeks from the beginning of the experiment, the growth of, duckweed was observed in the water bath" (page 5, lines 5 to 7 of the 1st Okamoto Declaration).

Thus, the non-treated microporous PP film cannot be used for controlling the rhizosphere environment (such as humidity and oxygen concentration) of a plant for a long time. Even when microporous films of hydrophobic materials other than PP is used (e.g., when a microporous PTFE film as described in **Sakai** is used), the same phenomenon as mentioned above occurs when the surface tension of water lowers.

Further, in Experiment 2 of the 1st Okamoto Declaration, the cultivation of arugula (rucola) seedlings was performed using the above-mentioned hydrophilized microporous PP film obtained by subjecting the same microporous PP film as used in Experiment 1 to hydrophilicity-imparting treatment as well as a non-porous PVA film. The results of the cultivation in Experiment 2 were as follows:

Microporous hydrophobic film

As shown in Fig. 3A (5 days, microporous hydrophobic film), it was clear that the microporous hydrophobic film had <u>transmitted tap water</u> so that the soil disposed on the film was <u>completely wetted</u>. Further, as shown in Fig. 4A, (16 days, microporous hydrophobic film), it was clear that the growth of the seedlings was <u>poor, as compared with Fig. 4B (16 days, PVA film)</u>.

PVA film

As shown in Fig. 3B (5 days, PVA film), the PVA was <u>not</u> wetted. Further, as shown in Fig. 4B (16 days, PVA film), the growth of the seedlings was <u>good</u>." (emphasis added) (page 7, last 2 paragraphs of the 1st Okamoto Declaration)

Thus, it is apparent that hydrophilized microporous PP film is <u>permeable to</u> liquid water and, hence, can<u>not</u> be used for controlling the rhizosphere environment (such as humidity and oxygen concentration) of a plant.

2nd Okamoto Declaration

In Experiment 1 of the <u>2nd</u> Okamoto Declaration, the cultivation of arugula (rucola) seedlings was performed using a cellophane (i.e., cellulose) film. The cellulose film is a non-porous hydrophilic film as in the case of the non-porous PVA film used in Experiment 1A above. However, since cellulose is biodegradable, the cellophane film used in Experiment 1 of the 2nd Okamoto Declaration was <u>broken</u> about 10 days after the start of the cultivation. Specifically, the results of cultivation were as follows:

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"However, in this case, some breakage of the cello-
phane film was observed thereafter, and water immer-
sion was caused in the inside of the film, to
thereby cause the <u>root rot</u> of rucola seedlings, as
shown in the photograph of the rucola seedlings af-
ter 31 days. Thereafter, the seedlings showed the
<u>apoptosis</u> thereof at 39 days after the beginning of
the cultivation." (emphasis added)(page 5, lines 5
to 11 of the 2nd Okamoto Declaration)

III. Results

Results of the evaluation of cultivated plants (arugula)

in Experiment 1A and Comparative Experiments 1A to 3A are sum-

marized in the following Table A.

Table A

	Type of film	Growth of plants	
		Height	Number of leaves
Experiment 1A (Present invention)	Non-porous PVA film	7 to 10 cm	6
Comparative Experiment 1A	micro-porous polypropylene film	3 to 7 cm	3
Comparative Experiment 2A	Silicone film	Withered	
Comparative Experiment 3A	Polyimide film	Withered	
Comparative Experiment 4A	Cellulose ace-tate	3 to 7 cm	3

Further, the results of Experiment 1 (cultivation of

pansy) and Experiment 2 (cultivation of arugula) of the 1st
Okamoto Declaration and the results of Experiments 2 and 3
(cultivation of arugula) of the 2nd Okamoto Declaration are
summarized in the following Table B.

Table B

	Type of film	Results
Experiment 1 of 1st Okamoto Declaration	Non-treated microporous PP film	About 2 months after the start of the cultivation, the soil on the film was immersed in water.
	Non-porous PVA film	Plant growth was good for over 3 months.
Experiment 2 of 1st Okamoto Declaration	Hydrophilized microporous PP film	The soil on the film was completely wetted, and the plant growth was poor.
	Non-porous PVA film	PVA film was not wetted and the plant growth was good.
Experiment 2 of 2nd Okamoto Declaration	Non-porous hydrophilic cellophane film	Cellulose film broke and the plant was withered.
Experiment 3 of 2nd Okamoto Declaration	Non-porous PVA film	Plant growth was good.

IV. Conclusion:

     From the above, it can be fairly concluded as follows.

     The system of the present invention is advantageous in
that, simply by supplying water in the water tank to a plant
through such a non-porous PVA film, the rhizosphere environ-

ment (such as humidity and oxygen concentration) can be easily
and favorably maintained for a long time even without directly
supplying water to the culture soil disposed on the film,
thereby enabling very rapid and full growth of a plant with
less amount of water (Experiment 1A shown in Table A, Experi-
ment 1 of the 1st Okamoto Declaration shown in Table B, and
Experiment 3 of the 2nd Okamoto Declaration shown in Table B).

On the other hand, a porous hydrophobic film (such as a
polypropylene film described in **Weder** et al. and a PTFE film
described in **Sakai**) cannot transmit therethrough a sufficient
amount of moisture (Comparative Experiment 1A shown in Table A,
and Experiment 1 of the 1st Okamoto Declaration shown in Table
B) and is likely to lose its impermeability to liquid water
during the cultivation of a plant, so that a porous hydropho-
bic film cannot be used for maintaining favorable rhizosphere
environment (such as moisture and oxygen content) for a long
time (Experiment 1 of the 1st Okamoto Declaration shown in Ta-
ble B).

Even if a microporous hydrophobic film is hydrophilized,
the resultant film freely passes water therethrough so that
such a hydrophilized film cannot be used for controlling the
rhizosphere environment of a plant (Experiment 2 of the 1st
Okamoto Declaration shown in Table B).

Further, the water vapor permselective films, such as a
silicone film, a polyimide film and a cellulose acetate film,
which are described in **Sakai** cannot supply sufficient amount
of water to the plant through the film (Comparative Experi-

- 19 -

ments 2A and 3A shown in Table A) so that the plant growth using any of such films is <u>poor</u>.

Furthermore, a cellophane film described in **Weder** et al. is <u>broken</u> when used in a manner as in the system of the present invention (Experiment 2 of the 2nd Okamoto Declaration shown in Table B).

From the above, it is apparent that the use of non-porous PVA film is essential for achieving the above-mentioned excellent effects of the system of the present invention.
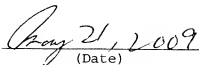
ATTACHMENT 1

DECLARATION OF TRANSLATOR

I, Maho Kaseki, c/o the Inoue & Associates of 3rd Floor, Akasaka Habitation Building, 3-5, Akasaka 1-chome, Minato-ku, Tokyo, Japan do solemnly and sincerely declare that I am conversant with the Japanese and English languages and that I have executed with the best of my ability this partial translation into English of Examined Japanese Utility Model Application Publication No. Hei 7-45169 (namely "Sakai" cited by the Examiner) and believe that the translation is true and correct.

The undersigned petitioner declares that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

May 21, 2009
(Date)

(signature)
(Signature)

1.   Page 1, column 1, line 1 to column 2, line 4:

[Registered Claims for Utility Model]

[Claim 1] An apparatus for cultivating plants in water areas
(such as seawater) unsuitable for cultivating plants, which
comprises: a framework capable of floating on the surface of
water containing non-volatile substances (such as salts)
which are harmful to plants, wherein said framework is made
of a floatation material or has a floatation material at-
tached thereto; and a waterproof moisture-permeable film
stretched on said framework to form the bottom of said appa-
ratus, wherein said film is used to feed water vapor to cul-
ture soil disposed inside said apparatus, said water vapor
being free of said non-volatile substances (such as salts)
which are harmful to plants.

[Claim 2] The apparatus according to claim 1, which further
comprises a water vapor permselective membrane, wherein said
membrane is attached to said waterproof moisture-permeable
film, thereby forming an integrated composite material.

[Detailed Description of the Utility Model]

"Task of the Utility Model"

     The present utility model is directed to an apparatus

- 1 -

for cultivating plants. The task of the present utility model is to provide a plant cultivating apparatus for use in lands and water areas unsuitable for cultivating plants, wherein said apparatus is capable of supplying water for cultivating and growing plants while effectively preventing adverse effects of harmful moisture present in the land or water area and of harmful gases generated from the harmful moisture. Further, the apparatus has a relatively simple structure which is easy to produce.

2.   Page 3, column 5, lines 9 to 16:

     Further, in the present utility model, if desired, water vapor permselective membrane 3 may be attached to the above-mentioned waterproof moisture-permeable film 2 to thereby form an integrated composite material. Examples of water vapor permselective membranes include a silicone membrane, a cellulose acetate membrane (a cellulose type membrane) and a polyimide membrane. Since these membranes are selectively permeable to water vapor, the composite material comprising the above-mentioned film 2 allows only water to pass therethrough, while preventing harmful substances from passing therethrough.

3. <u>Page 3, column 5, lines 27 to 32</u>:

As explained above, when methane gas and other gases
which are harmful to plants are present in drainage or the
like, the water vapor permselective membrane is used to pre-
vent the entry of such harmful components into the culture
soil disposed inside framework 1. In addition, as shown in
Fig. 4, gas permeation preventive material 11 is disposed on
the water surface at portions between plurality of frameworks
1 to prevent the diffusion of the harmful components from the
water surface.

4. <u>Page 3, column 5, lines 41 to 48</u>:

As waterproof moisture-permeable film 2 mentioned above,
it is preferred to use a polytetrafluoroethylene (PTFE) mem-
brane which is made porous by subjecting to an expansion
treatment, wherein the resultant porous film has a porosity
of from 40 to 95 %, a maximum pore diameter of from 0.1 to 15
μm, and a Gurley number of from 0.1 to 100 seconds. The po-
rous PTFE film exhibits not only excellent chemical resis-
tance, but also high heat resistance. Therefore, although
the porous PTFE is in the form of a film, it exhibits advan-
tageous durability. A preferred plant cultivation container
capable of sustaining the weight of the culture soil can be

obtained by attaching reinforcing material 6 made of resin
fibers, metals or the like to both the upper and lower sur-
faces of the film.

5. Page 3, column 6, lines 15 to 26:

    Surface of culture soil 7 is exposed at portions between
plants 9. Such surface of culture soil 7 may be covered with
vinyl sheet 8 in the manner depicted in Fig 2 to thereby pre-
vent the evaporation of moisture from the culture soil. Fur-
ther, vinyl sheet 8 will guide water from rainfalls and the
like to the periphery of plant 9 and feed the water to cul-
ture soil 7.
    It is apparent that the present utility model can be
used a preferred means for supplying water needed for plant
growth. However, it is also apparent that water requirement
of a plant will increase in accordance with the plant growth
and increasing plant size. When the water requirement in-
creases, the present utility model can be used as a means for
water saving. In this case, it is consequential to use the
present utility model in combination with the above-mentioned
conventional methods for supplying water or methods for water
saving.

ATTACHMENT 2

POLYMER HANDBOOK

FOURTH EDITION

Volume 2

Editors

J. BRANDRUP, E. H. IMMERGUT, and E. A. GRULKE

Associate Editors

A. ABE
D. R. BLOCH

Permeability and Diffusion Data

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A. INTRODUCTION

The transmission of molecules through polymer films is named "permeability". There are many dimensions and units found in the literature for the general expression "permeability". In this paper the permeability coefficient is used. It has the dimension

$$P = \frac{\text{(quantity of permeant)} \times \text{(film thickness)}}{\text{(area)} \times \text{(time)} \times \text{(pressure drop across the film)}}$$

and is the best definition for permeability.

The permeability coefficient, in a strict sense, is not only a function of the chemical structure of the polymer. It also varies with the morphology of the polymer and depends on many physical factors such as density, crystallinity, and orientation. However, the chemical structure of a polymer can be considered to be the predominant factor which controls the magnitude of the permeability coefficient.

The following general trends in permeability, as related to some influencing factors, may be useful for the proper interpretation of the tables:

Density can be regarded as a measure of the free volume between the molecules of the polymer structure. In general, the higher the density, the lower is the permeability.

Crystallinity of a semicrystalline polymer reduces the permeability significantly compared to the value of the corresponding amorphous polymer; i.e., the higher the degree of crystallinity, the lower the permeability. The crystallinity and the density of a polymer are strongly related. The higher the crystallinity the higher is the density of a given polymer.

Molecular mass of a polymer has been found to have little effect on the permeability of polymers, except at a very low range of molecular masses.

Orientation of polymer molecules reduces the permeability.

Crosslinking decreases the permeability, especially for higher degrees of crosslinking and for large molecular size permeants.

The method and degree of vulcanization has a significant effect on the permeability of elastomers.

Plasticizers increase the permeability.

Humidity increases the permeability of some hydrophilic polymers.

Liquid permeants have the same permeabilities as their corresponding saturated vapors, though higher permeabilities may occur especially if parts of the polymer are being dissolved.

Solution cast films have variable permeabilities depending upon the kind of solvent used and the drying technique. Poor solvents tend to yield films of higher permeability.

Fillers, usually inorganic fillers, decrease the permeability; however, the effect is complicated by the type, shape, and amount of filler and its interaction with the polymer.

Thickness of film does not, in principle, affect the permeability coefficient, the diffusion coefficient, and the solubility coefficient. In practice, different values may be obtained from films of variable thickness, which in turn may be due to differences in drawing, orientation, and crystallinity.

If a permeant does not interact with the polymer under investigation, the permeability coefficient is characteristic for the permeant–polymer system. This is the case with the permeation of many gases, such as H_2, He, N_2, O_2, and CO_2, through many polymers. On the other hand, if a permeant interacts with the polymer, the permeation coefficient is no longer a constant, and may depend on the special conditions of the measurement and the history of the polymer film. In such cases, a single value of the permeability coefficient does not represent the characteristic permeability of the polymer, and it is necessary to know the dependency of the permeability coefficient on all possible variables in order to obtain the complete profile of the permeability of the polymer.

In these cases, the transmission rate, which has the dimension

$$Q = \frac{\text{(quantity of permeant)}}{\text{(area)} \times \text{(time)}}$$

is often used for practical purposes. Since the transmission rate, Q, includes neither the pressure of the permeant nor the thickness of the polymer in its dimension, it is necessary to know either the pressure or the concentration of the permeant and the thickness of the polymer under the conditions of measurement.

For both P and Q, the quantity of permeant can be expressed by mass, moles, or gaseous volume at standard temperature and pressure. These can readily be converted from one unit to another.

The preferred SI unit of the permeability coefficient used in this book is

$$\text{unit of } P: \frac{\text{cm}^3(273.15 \text{ K}; 1.013 \times 10^5 \text{ Pa}) \times \text{cm}}{\text{cm}^2 \times \text{s} \times \text{Pa}}$$

where $(273.15 \text{ K}; 1.013 \times 10^5 \text{ Pa})$ means standard temperature and pressure (STP). Therefore permeability coefficients given in this paper are in the range of $10^{-11} - 10^{-16} \text{ cm}^3 \times \text{cm/cm}^2 \times \text{s} \times \text{Pa}$ for many polymers and permeants.

The mostly used units and their conversion factors are listed in Table B.

The permeation of molecules through flawless polymers occurs by the steps of dissolution of a permeant in the polymer and diffusion of the dissolved permeant. The product of the diffusion coefficient D and the solubility coefficient S is referred to as the permeability coefficient.

$$P = D \times S$$

Units of D and S used in these tables are

$$\text{unit of } D: \frac{\text{cm}^2}{\text{s}}$$

$$\text{unit of } S: \frac{\text{cm}^2(273.15 \text{ K}; 1.013 \times 10^5 \text{ Pa})}{\text{cm}^3 \times \text{Pa}}$$

The solubility coefficients cited in the following tables are often calculated by

$$S = \frac{P}{D}$$

The temperature dependence of the permeability coefficient P, the diffusion coefficient D, and the solubility coefficient S can be represented by

$$P = P_0 \times \exp(-E_P/RT)$$
$$D = D_0 \times \exp(-E_D/RT)$$

and

$$S = S_0 \times \exp(-E_S/RT)$$

Consequently

$$E_P = E_D + E_S$$

where E_P is the activation energy of permeation, E_D the activation energy of diffusion, and E_S the heat of solution. P_0, D_0, and S_0 are the pre-exponential factors. Values of E_P, E_D, and E_S are given in kJ/mol in the following tables. R is the gas constant (8.3144×10^{-3} kJ/K mol); T is the temperature in K. In the following tables the temperature range is given in which P_0, E_P, E_D, and E_S are relevant, as

far as the authors have reported it. The permeability coefficient can be determined for a given temperature by means of the pre-exponential factor P_0 and the activation energy of permeation E_P. In the following tables, permeability, diffusion, and solubility coefficients are listed for many polymers. The pre-exponential factor P_0, the activation energy of permeation E_P, the activation energy of diffusion E_D, and the heat of solution E_S are also given. The pre-exponential factors D_0 and S_0 can be determined by the following equations:

$$D_0 = D \times \exp(E_D/RT)$$

$$S_0 = S \times \exp(E_S/RT)$$

B. CONVERSION FACTORS FOR VARIOUS UNITS OF THE PERMEABILITY COEFFICIENT

From	Multiplication factors to obtain P in:		
	$\dfrac{[cm^3][cm]}{[cm^2][s][cm\ Hg]}$	$\dfrac{[cm^3][cm]}{[cm^2][s][Pa]}$	$\dfrac{[cm^3][cm]}{[m^2][day][atm]}$
$\dfrac{[cm^3][cm]}{[cm^2][s][cm\ Hg]}$	1	7.5×10^{-4}	6.57×10^{10}
$\dfrac{[cm^3][mm]}{[cm^2][s][cm\ Hg]}$	10^{-1}	7.5×10^{-5}	6.57×10^9
$\dfrac{[cm^3][cm]}{[cm^2][s][atm]}$	1.32×10^{-2}	9.87×10^{-6}	8.64×10^8
$\dfrac{[cm^3][mil]}{[cm^2][day][atm]}$	3.87×10^{-14}	2.90×10^{-17}	2.54×10^{-3}
$\dfrac{[in^3][mil]}{[100in^2][day][atm]}$	9.82×10^{-12}	7.37×10^{-15}	6.45×10^{-1}
$\dfrac{[cm^3][cm]}{[m^2][day][atm]}$	1.52×10^{-11}	1.14×10^{-14}	1
$\dfrac{[cm^3][cm]}{[m^2][day][bar]}$	1.54×10^{-11}	1.16×10^{-14}	.1.01
$\dfrac{[cm^3][cm]}{[cm^2][s][Pa]}$	1.33×10^3	1	8.75×10^{13}

C. TABLES

TABLE 1. PERMEABILITY COEFFICIENTS, DIFFUSION COEFFICIENTS, AND SOLUBILITY COEFFICIENTS OF POLYMERS

Units used in the tables are as follows: P, P_0 in cm^3 (273.15 K; 1.013×10^5 Pa) $\times$ cm/(cm$^2 \times$ s $\times$ Pa); D in cm^2/s; S in cm^3 (273.15 K; 1.013×10^5 Pa)/(cm$^3 \times$ Pa); E_P, E_D, E_S in kJ/mol; T in °C; (273.15 K; 1.013×10^5 Pa) means standard temperature and pressure (STP).

Polymer	Permeant	T	$P (\times 10^{13})$	$D (\times 10^6)$	$S (\times 10^6)$	Temp. range	$P_0 (\times 10^7)$	E_P	E_D	E_S	Refs.
1.1. POLY(ALKANES)											
Poly(ethylene) LLDPE	C_2H_4O	30	68.9		0.031		225				80
Poly(ethylene)	H_2	25	7.4	0.474	1.58						49
density 0.914 g/cm³. LDPE	D_2	25	6.6	0.476	1.38						49
	He	25	3.7	6.8	0.0544	5–60	4.62	34.8	24.7	10.1	16
	O_2	25	2.2	0.46	0.472	5–60	66.5	42.7	40.2	2.5	16
	Ar	25	2.1	0.36	0.571	5–60	174	45.2	42.3	2.9	16
	Ne	25	0.48	2.42	0.020						49
	Kr	25	2.15	0.169	1.28						49
	Xe	25	4.01	0.069	5.82						49
	CO_2	25	9.5	0.372	2.54	5–60	62.0	38.9	38.5	0.4	16

References page VI-568

Polymer	Permeant	T	$P (\times 10^{10})$	$D (\times 10^6)$	$S (\times 10^4)$	Temp. range	$P_0 (\times 10^7)$	E_P	E_D	E_S	Refs.
	CH_4	25	0.0237	0.0017	1.39	25–40	0.72×10^3	82.7	80.8	1.9	15
	CO_2	35	1.52	0.00747	20.4						86
Poly(vinyl alcohol)	He^c	20	0.00075								10
	H_2^c	25	0.00672								28
	D_2^c	100	0.0134								57
	N_2^c	14	0.0001								11
	N_2^c	25	0.248	0.045	0.53						11
	O_2^c	25	0.00665								28
	O_2^c	23	0.00005								59
	CO_2^c	25	0.00924								28
	CO_2^c	25	65.0								28
	H_2S^c	25	0.0052								28
	$C_2H_4O^c$	0	0.0015								37
	H_2O	25	5.25								98
Poly(vinyl benzoate)	H_2	25	6.55	1.93	0.34	20–60	0.0055	16.7	21.9	−5.2	65
		70	18.3	6.39	0.29	60–85	0.251	27.2	24.5	2.7	65
	He	25	8.67	6.17	0.11	20–60	0.00345	15.5	16.9	−1.3	65
		70	17.1	16.1	0.11	60–85	0.458	29.1	22.4	6.7	65
	Ne	25	1.51	1.08	0.14	20–60	0.00137	16.9	23.2	−6.3	65
		70	4.28	3.83	0.11	60–85	0.758	34.5	28.6	5.9	65
	Ar	25	0.358	0.033	1.08	20–60	0.0020	21.4	31.6	−10.1	65
		35	0.459	0.0491	0.93						86
		70	1.24	0.181	0.69	60–85	0.863	38.4	38.1	0.29	65
	Kr	25	0.192	0.0699	2.5	20–60	0.00188	22.8	38.4	−15.5	65
		70	0.712	0.049	1.45	60–85	2.565	43.1	50.7	−7.7	65
	Xe	25	0.071	0.00064	11.1	20–60	0.00723	28.6	46.0	−17.5	65
		70	0.43								65
	N_2	25	0.124	0.026	0.48	20–60	0.00104	22.4	33.0	−10.6	65
		70	0.463	0.158	0.29	60–85	1.26	42.3	45.2	−2.9	65
	O_2	25	0.715	0.079	0.91	20–60	0.00060	16.7	25.1	−8.5	65
		70	2.11	0.309	0.68	60–85	2.76	40.2	30.5	9.8	65
	CO_2	25	4.17	0.020	20.9	20–60	0.00200	9.6	32.9	−23.4	65
		35	4.74	0.030	16.2						86
		70	8.06	0.117	6.9	60–85	0.734	32.6	45.2	−12.5	65
Poly(vinyl butyral)	H_2O	25	608								98
Poly(vinyl-p-isopropylbenzoate)	He	25	8.93	15.5	0.0578	20–67	0.590	27.5	18.4	9.1	86
		80	49.9	51.9	0.096	67–95	0.537	27.3	23.5	3.7	86
	Ne	25	3.88	2.72	0.0585	20–67	0.00251	16.0	17.1	−1.1	86
		80	13.9	8.71	0.160	67–95	1.09	33.1	23.4	9.6	86
	Ar	25	1.90	0.668	1.15	20–67	0.00131	16.2	27.5	−11.3	86
		80	7.67	1.11	0.691	67–95	11.6	41.8	39.7	2.1	86
	Kr	25	0.940	0.0388	3.91	20–67	0.000248	13.8	32.2	−18.3	86
		80	6.25	0.393	1.61	67–95	40.6	46.1	47.3	−1.3	86
	Xe	25	0.00942	0.00579	16.5	20–67	0.00000289	14.2	36.1	−22.0	86
		80	4.62	0.0898	5.14	67–95	534.8	54.5	61.5	−7.0	86
	O_2	25	2.44	0.279	0.0546	20–67	0.00180	16.6	26.8	−10.4	86
		80	12.4	1.948	0.637	67–95	6.92	38.9	37.4	1.4	86
	N_2	25	0.647	0.115	0.550	20–67	0.000678	17.9	29.3	−11.4	86
		80	2.99	0.874	0.348	67–95	19.4	46.1	42.4	3.6	86
	CO_2	25	15.7	0.0760	20.6	20–67	0.000110	4.8	30.4	25.5	86
		80	32.9	0.638	5.17	67–95	3.57	34.0	43.9	−9.9	86
	CH_4	25	1.32	0.0462	2.84	20–67	0.000512	14.8	33.1	−18.3	86
		80	5.65	0.478	1.163	67–95	58.7	47.4	48.1	−0.6	86
Poly(vinyl-m-methylbenzoate)	Ar	35	0.642	0.0738	0.870						86
	CO_2	35	5.05	0.0361	14.0						86
Poly(vinyl chloride) unplasticized	He	25	1.5	2.8	0.055	25–80	0.212	29.9	20.7	9.2	32
	H_2	25	1.3	0.5	0.26	25–80	1.46	34.5	34.5	0	32
	Ne	25	0.29	0.25	0.12	25–80	0.274	34.1	31.5	2.6	32
	N_2	25	0.0089	0.0038	0.23	25–80	9380	69.0	61.9	7.1	32
	Ar	25	0.0086	0.0012	0.75	25–80	6.28	51.8	51.5	6.3	32
	Kr	25	0.0060	0.00041	0.54	25–70	24.2	55.3	62.8	−7.5	32
		80	0.14			75–90	8.85×10^5	86.6	128.5	−41.9	32
	O_2	25	0.034	0.012	0.29	25–80	179	55.8	54.6	1.2	32
	CO_2	25	0.12	0.0025	4.7	25–90	930	56.6	64.6	−7.8	32
	CH_4	25	0.021	0.0013	1.7	25–83	7950	56.2	70.3	−4.1	32
	H_2O	25	206	0.024	870	25–80	2.04	22.9	41.8	−18.9	32
	H_2S	25	0.14	0.000046	310						5
	NH_3	20	3.7								5
	C_3H_6O	20	4.4	0.0013	330						80
unplasticized (Pentaform Type TH 170/01)	He	35	2.52								75
	N_2	35	0.00709	0.00188							75
	Ar	35	0.0277	0.00339							75
	CO_2	35	0.182	0.00145							75
	CH_4	35	0.00810								75

Polymer	Permeant	T	P (×10¹³)	D (×10⁸)	S (×10⁴)	Temp. range	P_s (×10⁷)	E_P	E_D	E_S	Refs.
	C_3H_6	25	0.0473	0.00013	36.2						9
	C_3H_8	25	0.0063	0.000021	29.6						9
Ethyl cellulose	He	25	40.1	2.21	1.8						9
	H_2	20	65.3								10
	N_2	25	3.32	0.233	1.43						9
	O_2	25	11.0	0.639	1.73						9
	Ar	25	7.65	0.403	1.88						9
	CO_2	25	84.8	0.565	15.0						9
	SO_2	25	198	0.0734	270						9
	NH_3	25	196	0.146	363						9
	H_2O	25	6700	0.0286	23400						9
	C_2H_6	25	6.9	0.019	36.3						9
	C_2H_6	30	10.0								79
	C_2H_6	40	10.3								79
	C_2H_6	50	12.2								79
	C_2H_6	60	14.9								79
	C_2H_6	70	20.1								79
	C_3H_8	25	2.78	0.00293	94.7						9
	C_3H_8	30	4.73								79
	C_3H_8	40	5.32								79
	C_3H_8	50	6.36								79
	C_3H_8	60	9.05								79
	C_3H_8	70	10.8								79
	$n\text{-}C_4H_{10}$	25	2.9	0.00146	199						9
	$n\text{-}C_4H_{10}$	30	4.20								79
	$n\text{-}C_4H_{10}$	40	6.30								79
	$n\text{-}C_4H_{10}$	50	7.43								79
	$n\text{-}C_4H_{10}$	60	9.77								79
	$n\text{-}C_4H_{10}$	70	11.4								79
	$n\text{-}C_5H_{12}$	25	2.78	0.00138	201						9
	$n\text{-}C_6H_{14}$	25	5.75	0.00124	462						9
(Bhoori 610)											
	$C_2H_4O^f$	30	308								37

a Thickness 0.29 mm.
b Thickness 0.64 mm.
c Relative humidity 0%.
d Relative humidity 100%.
e Plasticizer was low-molecular-weight poly(trifluorochloroethylene)

f 3.5% aqueous sodium chloride solution (simulated sea water).
g The % bromination refers to 100 times the number of bromine atoms per repeat unit.
h Relative humidity 43%
i Relative humidity 76%.
j Plasticized.

TABLE 2. PERMEABILITY COEFFICIENTS OF SIX DIFFERENT FLUORINATED HYDROCARBONS THROUGH POLYMERS[a]

Polymer	$CFCl_3$ (24.5°C)	CF_2Cl_2 (20°C)	CF_4 (20°C)	$CHFCl_2$ (20°C)	CHF_2Cl (20°C)	$CF_2Cl\text{-}CF_2Cl$ (20°C)	N_2 (20°C)
Poly(ethylene) low density	37.5	152	2.03	1.88	0.795	0.212	0.914
high density	9.75	30	0.673	0.374	0.106	0.0683	0.219
high density, drawn	3.38	4.35	0.326	0.161	0.0266	0.0336	0.133
Poly(propylene)	4.88	137	0.132	0.00338	0.0018	0.00728	0.151
Poly(vinyl chloride) (Genotherm UG), unplasticized	0.697	0.00668	0.00585	0.0016	0.0016	0.00503	0.0247
Poly(vinyl chloride) (Guttagena T52), plasticized	656	63.8	1.88	0.359	0.185	0.054	0.0649
Poly(oxyethyleneoxyterephthaloyl) [Poly(ethylene terephthalate)] (Hostaphan)	0.00188	0.00135	0.0016	0.00135	0.00165	0.0039	0.00343
Poly(imino-1-oxohexamethylene) (Supronyl S)	0.0315	0.0329	0.0111	0.00623	0.00803	0.00923	0.0075
Poly(imino-1-oxohexamethylene) (Supronyl N), plasticized	52.5	3.6	0.254	0.00473	0.00143	0.00225	0.0133

a Ref. 82; P in cm³ × cm/(cm² × s × Pa) × 10⁻¹³.

TABLE 3. PERMEABILITY COEFFICIENTS OF VARIOUS ORGANIC COMPOUNDS THROUGH LOW-DENSITY POLY(ETHYLENE)[a]

Permeant	0°C	21.1°C	54.4°C	73.9°C
Acetaldehyde	1.34	2.36		
Acetanilide		0.008	0.16	1.34
Acetic acid	0.14	1.22	25.9	119

D. REFERENCES

1. R. Ash, R. M. Barrer, D. G. Palmer, Polymer, **11**, 421 (1970).

2. R. M. Barrer, H. T. Chio, J. Polym. Sci, C, **10**, 111 (1966).

3. J. A. Barrie, B. Plott, Polymer, **4**, 303 (1963).

4. W. W. Brandt, J. Polym. Sci., **41**, 415 (1959).

5. V. L. Braunisch, H. Lenhart, Kolloid-Z., **177**, 24 (1961).

6. J. Crank, C. Robinson, Proc. Roy. Soc. (London) A, **204**, 549 (1951).

7. P. M. Hauser, A. D. McLaren, Ind. Eng. Chem. Int. Ed., **40**, 112 (1948).

8. W. Heilman, V. Tammela, J. A. Meyer, V. Stannett, M. Szwarc, Ind. Eng. Chem., **48**, 821 (1956).

9. P. Y. Hsieh, J. Appl. Polym. Sci., **7**, 1743 (1963).

10. Y. Ito, Kobunshi Kagaku, **18**, 124 (1961).

11. Y. Ito, Kobunshi Kagaku, **18**, 158 (1961).

12. Y. Iyengar, J. Poly. Sci. B, **3**, 663 (1965).

13. D. Jeschke, Ph. D. Thesis, Mainz, 1960.

14. P. Mears, J. Am. Chem. Soc., **76**, 3415 (1954).

15. P. Mears, Trans. Faraday Soc., **53**, 101 (1957).

16. A. S. Michaels, H. J. Bixler, J. Polym. Sci., **50**, 413 (1961).

17. A. S. Michaels, W. R. Vieth, J. A. Barrie, J. Appl. Phys., **34**, 1 (1963).

18. A. S. Michaels, W. R. Vieth, J. A. Barrie, J. Appl. Phys., **34**, 13 (1963).

19. A. W. Myers, V. Stannett, M. Szwarc, J. Polym. Sci., **35**, 285 (1959).

20. A. W. Myers, V. Tammela, V. Stannett, M. Szwarc, Mod. Plastics, **37** (10), 139 (1960).

21. A. W. Myers, J. A. Meyer, C. E. Rogers, V. Stannett, M. Szwarc, Tappi, **44**, 58 (1961).

22. F. J. Norton, J. Appl. Polym. Sci., **7**, 1649 (1963).

23. R. A. Pasternak, M. V. Christenson, J. Heller, Macromolecules, **3**, 366 (1970).

24. R. A. Pasternak, G. L. Burns, J. Heller, Macromolecules, **4**, 470 (1971).

25. D. R. Paul, A. T. DiBenedetto, J. Polym. Sci. C, **10**, 17 (1965).

26. R. W. Roberts, K. Kammermeyer, J. Appl. Polym. Sci. **7**, 2183 (1963).

27. G. Rust, F. Herrero, Materialprüfung, **11** (5), 166 (1969).

28. V. L. Simril, A. Hershberger, Modern Plastics, **27** (11), 95 (1950).

29. V. Stannett, J. L. Williams, J. Polym. Sci. C, **10**, 45 (1966).

30. V. Stannett, North Carolina State University unpublished data.

31. R. L. Taylor, D. B. Hermann, A. R. Kemp, Ind. Eng. Chem. Int. Ed., **28**, 1255 (1936).

32. B. P. Tikhomirov, H. B. Hopfenberg, V. T. Stannett, J. L. Williams, Makromol. Chem., **118**, 177 (1968).

33. G. J. Amerongen, J. Appl. Phys., **17**, 972 (1946).

34. G. J. Amerongen, J. Polym. Sci., **2**, 381 (1947).

35. G. J. Amerongen, J. Polym. Sci., **5**, 307 (1950).

36. G. J. Amerongen, Rubber Chem. Technol., **37**, 1065 (1964).

37. R. Waack, N. H. Alex, H. L. Frisch, V. Stannett, M. Szwarc, Ind. Eng. Chem., **47**, 2524 (1955).

38. J. L. Williams, V. Stannett, J. Appl. Polym. Sci., **14**, 1949 (1970).

39. H. Yasuda, V. Stannett, J. Polym. Sci., **57**, 907 (1962).

40. H. Yasuda, V. Stannett, J. Macromol. Sci. B, **3** (4), 589 (1969).

41. H. Yasuda, Kj. Rosengren, J. Appl. Polym. Sci., **14**, 2839 (1970).

42. M. Salame, J. Polym. Sci. Symp., **41**, 1 (1973).

43. H. Platenius, Modern Packaging, **17**, 2103 (1943).

44. L. Phan Thuy, A. Lukaschov, J. Springer, Colloid Polym. Sci., **261**, 973 (1983).

45. M. Sefcik, J. Schaefer, F. May, D. Raucher, J. Polym. Sci., **21**, 1041 (1983).

46. N. Minoura, S. Tani, T. Nakagawa, J. Polym. Sci., **22**, 833 (1978).

47. S. Sczi, J. Springer, Colloid Polym. Sci., **259**, 1170 (1981).

48. E. Sacher, J. Polym. Sci., **28**, 1535 (1983).

49. H. Miyake, M. Matsuyama, K. Ashida, K. Watanabe, J. Vac. Sci. Technol. A-1, **3**, 1447 (1983).

50. P. T. Delassus, D. J. Grieser, J. Vinyl Technol. **2** (3), 195 (1980).

51. W. H. Yang, V. F. Smolen, N. A. Peppas, J. Membr. Sci., **9**, 53 (1981).

52. P. E. Cassidy, T. M. Aminabhavi, J. C. Brunson, Rubber Chem. Technol., **56**, 357 (1983).

53. N. Y. Yan, R. M. Felder, W. J. Koros, J. Polym. Sci., **25**, 1755 (1980).

54. H. Fitz, Kunststoffe, **70**, 27 (1980).

55. T. Duncan, W. J. Koros, R. M. Felder, J. Polym. Sci., **28**, 209 (1983).

56. E. Sacher, J. R. Susko, J. Polym. Sci., **27**, 3893 (1982).

57. D. H. W. Carstens, E. P. Ehart, J. Polym. Sci., **29**, 261 (1984).

58. H. Kenbishi, Int. Polym. Sci. Technol., **8** (4), (1981).

59. H. Schuch, Kautschuk, Gummi, Kunststoffe, **33** (9), (1980).

60. R. Light, R. Seymour, Soc. Plast. Eng., **29**, 417 (1983).

61. H. Braunisch, B. Hoffmann, Kältetechnik, **13** (2), 59 (1961).

62. M. Solame, S. P. E. Trans., **1**, 153 (1961).

63. H. Bent, J. Polym. Sci., **24**, 387 (1957).

64. J. Flynn, Polymer, **23**, 1325 (1982).

65. T. Hirose, K. Mizoguchi, Y. Kamiya, J. Polym. Sci., **30**, 401 (1985).

66. E. Sacher, J. Susko, J. Polym. Sci., **24**, 1997 (1979).

67. W. Koros, J. Wang, R. Felder, J. Polym. Sci., **26**, 2805 (1981).

68. E. Sacher, R. Susko, J. Polym. Sci., **23**, 2355 (1979).

69. A. L. Andrady, M. D. Sefcik, J. Polym. Sci., **21**, 2453 (1983).

70. A. L. Andrady, M. D. Sefcik, J. Polym. Sci., **22**, 217 (1984).

71. R. W. Macdonald, R. Y. M. Huang, J. Polym. Sci., **26**, 2239 (1981).

72. L. H. Wang, R. S. Porter, J. Polym. Sci., **22**, 1645 (1984).

73. S. Pauly, HOECHST AG, Werk Kalle, unpublished data.

74. P. S. Holden, G. A. J. Orchard, I. M. Ward, J. Polym. Sci., **23**, 709 (1985).

ATTACHMENT 3

Permeability of
Polymeric Films to Gases[1]

by V. L. SIMRIL[††] AND A. HERSHBERGER[††]

The permeabilities of 21 polymeric films to oxygen, hydrogen, carbon dioxide, nitrogen, ammonia, hydrogen sulphide, and sulfur dioxide, both dry and moist, were studied. The data are presented in terms of a permeability constant P* and are interpreted in terms of the structures and physical properties of the films and the gases. In general, it may be said that gas permeation increases with any decrease in the bonding forces between the polymer molecules of the film and with any increase in the attractive forces between film and gas. Thus, highly polar, strongly bound polymers are less permeable to non-polar gases than are the less polar, weakly bound polymers. The introduction of side chains onto the main polymer chains, the introduction of plasticizers, and the presence of water all tend to increase permeability. Certain significant deviations from this general rule are noted and discussed.

THE selective permeability of polymeric films to certain gases is becoming commercially important. Recently, several investigators, (1–6)* using several experimental techniques, have reported permeability data for a number of film-gas combinations. The investigations reported here were undertaken to obtain quantitative data on rates of gas transmission through a number of thin polymeric films and to interpret the data in terms of film and gas molecular structure and the effect of water and plasticizer content of the films.

Preparation of Films

Twenty-one polymeric films were investigated in this study. They are listed with their compositions and preparations in Table I. In general, they were prepared by the same procedures as were given in the first (7) of these two articles.

Reagents

The gases used in this study were purchased in commercial cylinders from a commercial source (8) and were used without further purifica-

tion. The purities quoted by the manufacturer in terms of percentage ware as follows:

Anhydrous ammonia	
(NH₃)	
Carbon dioxide (CO₂)	99.0
Hydrogen (H₂)	99.8
Hydrogen sulphide (H₂S)	99.9
Nitrogen (N₂)	99.9
Oxygen (O₂)	99.6
Sulfur dioxide (SO₂)	99.7

[1]—Gas transmission units used to obtain permeability data. Standard model at left; modified at right

All of the gas permeability data reported here was obtained with a standard General Foods gas-transmission instrument or with a modified instrument constructed to our specifications. These two instruments are pictured in Fig. 1, the standard model being on the reader's left. Schuman (4) and Elder (5) describe the standard model and the method of making gas transmission measurements with it in detail. The modified model (schematically illustrated in Fig. 2) operates on the same principle as the standard, but provides higher sensitivity over a greater range of permeability rates through the use of an inclined manometer and a larger reservoir space on the film's vacuum side.

The major portion of the data was obtained at 24 to 25° C. The testing temperature was not permitted to
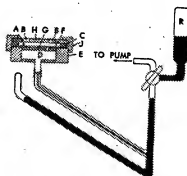
2—Sketch of modified model. A) Filter paper; B) gas entrance and exit ports; C) rubber gasket; D) gas chamber; E) block; F) film; G) film support; H) sealing disk; J) clamping ring; and R) mercury reservoir

vary more than ± 0.5° C. from the mean for any particular test. The pressure of the gas above the film was determined by the atmospheric pressure and did not vary more than ± 1 mm. (Hg) during any test. The

film being tested was protected from moisture by drying towers in both the incoming and outgoing gas lines except when the incoming of water in the gas was being determined. In such cases, the incoming gas was conditioned to the desired humidity by passing through bubble bottles containing saturated salt solutions. The observed exit pressure of the gas was then corrected for the partial pressure of the water vapor and for the pressure drop in the exit gas line.

All gas permeability data obtained in this study are reported here in terms of the permeability constant P* which is defined as the number of moles of gas passing through one sq. cm. of film, one cm. thick, per sec. per cm. (Hg) vapor-pressure difference across the film. Vapor pressure changes on the vacuum side of the film were recorded until P* reached a constant value. The vapor-pressure differences across the films at the time at which P* became constant varied

between a minimum of 67 cm. (Hg) and a maximum of 74 cm. (Hg) for the different film-gas combinations. Check determinations were made on each combination using a fresh sample of film each time. Values of P* for check determinations varying more than 10% were not included in the calculations.

Experimental Results

All of the gas transmission data obtained in this study are reported as permeability constants in Tables II through VIII. P* may be converted to practical units such as cc/sq.in./hr., if desired, for any particular gas at any pressure differential across a film of established thickness.

The mechanisms by which gases may pass through films are thought to be the same as those by which vapors penetrate films. Briefly, according to the generally accepted picture, the gas may penetrate existing holes in the polymer structure or holes which are opened

Table I—Film Composition and Preparation

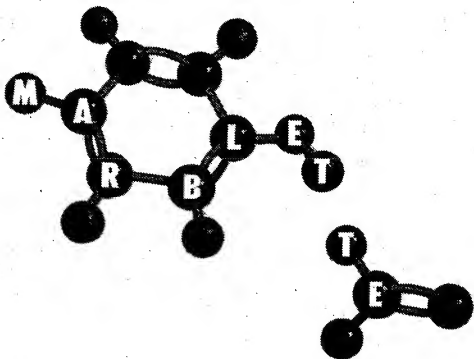| Film No.	Composition	Preparation
I	Regenerated cellulose; no plasticizer	Viscose process
II	Regenerated cellulose; 12% ethylene glycol plasticizer	Viscose process
III	Regenerated cellulose; 17% ethylene glycol plasticizer	Viscose process
IV	Regenerated cellulose; 14% glycerol plasticizer	Viscose process
V	Regenerated cellulose; 22% glycerol plasticizer	Viscose process
VI	Regenerated cellulose; no plasticizer	Deacetylated cellulose acetate film
VII	Regenerated cellulose; no plasticizer	High solids viscose—heat coagulated and regenerated in acid-salt solution
VIII	Regenerated cellulose; 18% glycerol plasticizer; coated both sides with 3 gm./sq. meter of nitrocellulose-wax moisture-proof coating	Viscose process
IX	Regenerated cellulose; 22% glycerol plasticizer; coated both sides with 6 gm./sq. meter of vinylidene chloride/acrylonitrile (90/10 weight ratio) copolymer moistureproof coating	Viscose process
X	Vinyl butyral/vinyl alcohol (89/11 mole ratio) copolymer	Cast from toluene/isopropanol solution
XI	Vinyl chloride/diethyl fumarate (95/5 weight ratio) copolymer	Cast from toluene/methyl ethyl ketone solution
XII	Nylon; 66/610/6 polyamide (40/30/30 weight ratio)	Cast from isopropanol/water solution
XIII	Rubber hydrochloride	Cast from chlorinated hydrocarbon solution
XIV	Vinylidene fluoride polymer	Cast from dimethyl formamide solution
XV	Vinyl alcohol polymer; no plasticizer	Cast from water solution
XVI	Vinylidene chloride/vinyl chloride (85/15 weight ratio) copolymer	Melt extruded
XVII	Polythene (ethylene polymer)	Cast from xylene solution
XVIII	Chlorinated polythene (33% chlorine by weight)	Cast from xylene solution
XIX	Chlorinated polythene (36.7% chlorine by weight)	Cast from xylene solution
XX	Chlorinated polythene (40.6% chlorine by weight)	Cast from xylene solution
XXI	Ethyl cellulose (48.3% ethoxyl) plasticized with 15% of butyl phthalyl butyl glycolate	Cast from toluene/ethanol solution

Table II—Permeability of Cellulose Film I

Gas	Temp.	Mol. wt.	Dipole moment* Debye units	P*×10⁹
	°C.			
H₂	24.3	2	0	2.81
NH₃	25.3	17	1.49	7.04
N₂	25.0	28	0	1.43
O₂	24.6	32	0	0.95
H₂S	27.8	34	0.95	0.51
CO₂	24.3	44	0	2.10
SO₂	28.1	64	1.61	0.77

*Smyth, C. P., *Dielectric Constant and Molecular Structure* New York: Reinhold Publishing Corp.

momentarily by thermal action, or the gas may dissolve in the film at one surface and evaporate from the film at the opposite surface. Inasmuch as gases are generally less soluble in films at room temperature than are vapors, transport by solution should not be such an important factor as it is for vapors.

The work reported here was concerned with correlating the structures of gases and of various polymer films with permeability rates. The data may conveniently be considered under two headings: regenerated cellulose films and other

Formula for Success

polymeric films. Such an arbitrary separation does not imply that both types of film do not obey similar laws of permeation, but is made because a greater variety of modifying factors was introduced into the investigation conducted on cellulose film permeability.

Cellulose Films

Effect of Gas Structure on Permeability—The permeability of re-generated cellulose film containing no plasticizer (see Film I in Table I) to seven dry gases is summarized in Table II.

The permeability of dry cellophane to gases is of the order of 10,000 times less than it is to vapors (see the preceding article of this series). This indicates that the cellophane structure is relatively compact and free of holes. There is a rough inverse correlation between the size of the gas molecules and their permeation rates. Remembering that polar cellulose should more readily dissolve polar molecules than non-polar molecules, the enhanced permeability of cellophane to ammonia and sulfur dioxide becomes understandable. On the basis of molecular size and polarity, the transmission rate of carbon dioxide appears to be too high. The incorporation of water in cellulose greatly increases carbon dioxide transmission (as shown in Table IV) and

Table III.—Gas Permeability of Structurally Dissimilar Cellophanes at 0% Relative Humidity

Film No. and type	P^* x 10^{17}	
	O_2	CO_2
I Regenerated cellulose	0.88	2.10
VI Deacetylated cellulose acetate sheet	4.12	4.34
VII Heat-coagulated viscose cellulose	5.46	.....

it is possible that a very small amount of water, inadvertently allowed to remain in the cellophane, is responsible for the high P^* value. In this event, P^* for carbon dioxide must be considered correct only as to order of magnitude. It is practically impossible to secure completely dry cellulose.

Effect of Film Structure on Permeability—X-ray diffraction, water absorption, and physical property

data (9) indicate that the physical structure of a cellulose sheet may be modified by the technique used in preparing it. An attempt was made to determine whether or not these structural changes would be reflected in gas transmission rates. The data of Table III indicate that three different cellulose films, normally thought to be quite different structurally, all exhibit gas transmission rates of the same order of magnitude.

Even the differences in P^* exhibited by these films may be due to mechanical flaws in the film: The best obtainable samples of the experimental deacetylated cellulose acetate and heat-coagulated films contained some thin spots and bubbles. However, the greater permeability of the experimental films compared to the machine-cast cellophane is in line with the less ordered structure assigned to them from water absorption and x-ray diffraction data.

Effect of the Presence of Water Vapor on Permeability—Cellulose films sorb water from gases containing water vapor. This phenomenon might be expected to affect the rate of transmission of a gas through a cellophane film in two ways. Thus, absorbed or adsorbed water might act as active centers for gas adsorption and increase gas permeation by a process of solution and evaporation. Also, the physical structure of cellulose is changed by sorbed water. Some of the active hydroxyl groups which, when water-free, would aid transmission of gases might be covered or blocked by the water and thus decrease gas transmission. On the other hand, the process of sorbing water causes the cellulose structure to expand and weakens the intermolecular forces to such an extent that the number of existing and potential holes available for gas transmission is increased. It might be expected that the permeability of cellulosic films to most gases would be increased by increasing the water content of the film. The data of Table IV substantiate this expectation.

The data in Table IV show clearly that the increase of permeability of a wet film over a dry film is closely related to the solubility of the permeant gas in water. It is obviously necessary to know the

relative humidity of a gas and its solubility in water before calculating its rate of permeation through a cellulose film.

Effect of Plasticizers on Permeability—It was demonstrated in the preceding article of this series that plasticizers may either increase or decrease the vapor permeability of a film. It was postulated that an increase was brought about by the spreading effect of the plasticizer on the polymer chains and, in some cases, by the solution of the vapor in the plasticizer. On the other hand,

Table IV.—Gas Permeability of Wet Regenerated Cellulose Film I at 24.5° C.

Gas	S^a	P^* x 10^{17} at various relative humidities			
		0%	43%	79%	100%
H_2	0.018	2.81	7.14	14.50	35.60
O_2	0.028	0.95	3.19	3.96	5.18
N_2	0.014	1.43	3.02	3.33	8.20
CO_2	0.770	2.10	5.80	32.10	114.50
NH_3	632.000	7.04	.....	.....	79,000.00
SO_2	33.400	0.77	.....	.....	16,900.00
H_2S	2.310	0.51	.....	.....	253.00

^{a} S is volume of gas (S.T.P.) dissolved in 1 volume of water when the pressure of the gas is 760 mm. Data from Lange's Handbook of Chemistry, 4th edition (1941).

a decrease was assumed to be caused by the blocking effect of the plasticizer in filling holes and adsorbing on active polymer groups which otherwise would be available for vapor solution. It would be reasonable to assume that plasticizers would have the same effects on gas transmission. The data of Table V indicate that plasticized regenerated cellulose is always more permeable to gases than unplasticized cellulose film, indicating that any blocking effect present is less important than chain spreading and/or gas solution due to plasticizer.
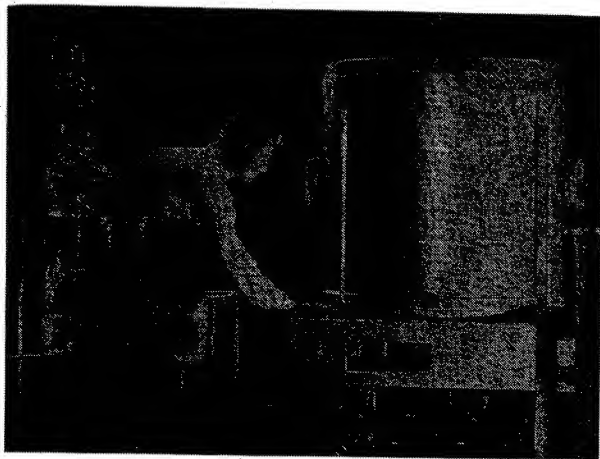
Measured by the extent to which they increase permeability, ethylene glycol and glycerol are roughly equivalent. The data taken at 100% relative humidity indicate that plasticized regenerated cellulose sorbs water more advantageously, from the standpoint of providing a diffusion path for gases, than does unplasticized regenerated cellulose. In normal practice, one is always concerned with a more or less moist gas and a plasticized film. For this

Table V.—Gas Permeability of Plasticized Regenerated Cellulose Films

Film Type	Plasticizer % of dry film wt.	Relative humidity %	H_2	O_2	N_2	CO_2	SO_2	H_2S
					$P^* \times 10^{10}$			
I None		0	2.81	0.95	1.43	2.10	0.77	0.51
I None		100	35.60	5.18	8.20	114.00	......	253.00
IV Glycerol	14	0	3.63	3.22	2.03	3.92	......	......
V Glycerol	22	0	6.60	4.51	3.45	4.98	33.6	1.00
V Glycerol	22	100	......	546.00	......	754.00	......	......
II Ethylene glycol	12	0	3.04	2.91	1.76	3.43	......	......
III Ethylene glycol	17	0	5.24	......	3.03	3.51	......	......

reason, it is imperative to know the plasticizer content of the film and the moisture contents of film and gas in solving any gas permeability problem.

Effect of Coatings on Regenerated Cellulose Permeability—The gas permeability of dry, plasticized, uncoated regenerated cellulose is less than that of most of the other film-forming polymers studied (see Tables V and VII). As a consequence, it would be reasonable to expect that the cellulose portion of polymer-coated cellophane sheets would be the permeability rate controlling portion. This would be particularly true of films coated with nitrocellulose-based coating. Cellulose derivatives are generally more permeable to gas and vapors than cellulose. The incorporation of wax, plasticizer, and resins in the coating further increases permeability, probably by disrupting any ordered existence the nitrocellulose molecules may have enjoyed otherwise. On the other hand, vinylidene chloride copolymers are almost as gas impermeable as dry regenerated cellulose, but, as thin coatings, they could not be expected to increase the over-all impermeability of the regenerated cellulose film to any appreciable extent.

The above discussion considers only dry gases. Inasmuch as water vapor penetrates all so-called "moistureproof" coatings at a measurable rate, sooner or later equilibrium between the water vapor in the diffusing gas and the cellulose base sheet will be attained. When equilibrium is reached, the gas transmission rate will be much higher unless a relatively gas-impermeable coating has been used.

The data of Table VI are in line with expectations. Wet, plasticized regenerated cellulose film V is highly permeable to carbon dioxide and oxygen. The nitrocellulose-based coating of film VIII decreases this permeability somewhat, but the effect of the water is still large. The permeability of the vinylidene chloride/acrylonitrile-coated film IX to wet gases is relatively quite small indicating that the coating (which is not much affected by water) has become the real obstacle confronting gas transmission.

Non-Cellulosic Films

The permeabilities of 12 non-cellulosic films to dry oxygen and carbon dioxide and to moist carbon dioxide were determined. The data are summarized in Table VII together with some data on hydrogen, nitrogen; and information on hydrogen sulfide.

The data of Table VII represent a spectrum of permeability ranging from unplasticized regenerated cellulose, polyvinyl alcohol, and vinylidene chloride/vinyl chloride on the low side to polythene, vinyl butyral/vinyl alcohol copolymer, and plasticized ethyl cellulose on the high side. The variation in permeability appears to be connected to variations in the structure and properties of the polymers and gases. Apparently, for gas permeability, the intermolecular attractive forces of the polymer film are quite important. If these forces are strong, the polymer chains should be held tightly together and it will be difficult for holes to exist through which gas molecules may pass. This hypothesis implies that the gas molecules will have little effect on the interchain bonds of the polymer. As an illustration, it is interesting to observe that dry polyvinyl alcohol, whose interchain forces are strong, exhibits low permeability both to the polar hydrogen sulfide molecule and the non-polar hydrogen and oxygen molecules. On the other hand, polythene can be held together only by weak van der Waal's forces, and it is highly permeable to both polar and non-polar gases. The presence of side chains on the main chains or of plasticizer between polymer molecules would be expected to decrease polymer intermolecular forces or to increase the number of paths available to gases in some fashion. Evidence that this does happen is available in the relatively high permeability of such films.

A comparison of the gas and vapor permeability of a few typical films provides a clue to the importance to permeability of the interaction (adsorption and intermolecular bond breaking) of polymer and diffusing molecule.

In the examples listed in Table

Table VI.—Permeability of Coated Regenerated Cellulose Films

Film No. and type	Relative humidity %	H_2	O_2	CO_2	SO_2
			$P^* \times 10^{10}$		
V Uncoated regenerated cellulose with 22% glycerol plasticizer	0	6.60	4.51	4.98	1.00
	100	......	546.00	754.00	......
VIII Regenerated cellulose with 18% glycerol plasticizer coated with a nitrocellulose-based moistureproof coating	0	6.53	3.45	5.59	......
	100	......	190.00	......	......
IX Regenerated cellulose with 22% glycerol plasticizer coated with vinylidene chloride/acrylonitrile (90/10) copolymer moistureproof coating	0	......	5.30	6.84	1.84
	100	......	12.70	13.70	11.47

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Table VII.—Permeability of Plastic Films to Gases

Film No. and Composition	Relative humidity	H_2	O_2	N_2	CO_2	H_2S
				$P^* \times 10^9$		
		%				
I Regenerated cellulose; no plasticizer	0	2.81	0.95	1.43	2.10	0.51
	100	35.60	5.18	8.20	114.00	253.00
V Regenerated cellulose; 22% glycerol plasticizer	0	6.60	4.51	3.45	4.98	1.00
	100	......	546.00	......	754.00	......
X Vinyl butyral/vinyl alcohol (89/11 mole ratio copolymer	0	4250.00	464.00	......	2280.00	2670.00
	100	......	......	......	1720.00	2940.00
XI Vinyl chloride/diethyl fumarate (95/5 weight ratio) copolymer	0	1040.00	50.60	......	169.00	......
	100	......	51.40	......	281.00	......
XII Nylon; 66/610/6 polyamide (40/30/30 weight ratio)	0	......	14.50	......	25.3	......
	100	......	......	......	261.00	......
XIII Rubber hydrochloride	0	......	42.50	......	139.00	......
	100	......	......	......	202.00	......
XIV Vinylidene fluoride polymer	0	184.00	24.40	......	160.00	......
	100	......	......	......	162.00	......
XV Vinyl alcohol polymer; no plasticizer	0	4.00	3.96	......	5.50	3.10
	100	......	......	......	38,700.00	......
XVI Vinylidene chloride/vinyl chloride (85/15 weight ratio) copolymer	0	......	5.96	......	5.89	......
	100	......	......	......	19.60	......
XVII Polythene (ethylene polymer)	0	2210.00	708.00	225	2740.00	6620.00
	43	1980.00	685.00	167	2580.00	7750.00
	100	......	839.00	......	3820.00	......
XVIII Chlorinated polythene (33% chlorine by weight)	0	......	77.80	......	276.00	......
	100	......	......	......	434.00	......
XIX Chlorinated polythene (36.7% chlorine by weight)	0	......	75.90	......	228.00	......
XX Chlorinated polythene (40.6% chlorine by weight)	0	......	45.90	......	127.00	......
XXI Ethyl cellulose (48.3% ethoxyl) plasticized with 15% of butyl phthalyl butyl glycolate	0	......	3470.00	......	21,200.00	......
	100	......	......	......	22,500.00	......

also quite significant that those gases which are most easily condensed (H_2S and CO_2) behave more nearly like vapors, with respect to permeation, than do the difficultly condensable gases, namely: H_2, O_2, and N_2.

It will be remembered that in the case of regenerated cellulose the addition of plasticizer or water appeared always to increase gas permeability. That water may have the same effect in non-cellulosic films may be seen from the data of Table VII. However, in the cases of some highly permeable films, water appears to block gas diffusion. Polythene, which absorbs water in quantities of water at high relative humidities, becomes less permeable as some water is added and then more permeable as it becomes saturated. Vinyl butyral/vinyl alcohol copolymer when saturated with water is less permeable to carbon dioxide but more permeable to hydrogen sulfide than when dry. Perhaps in the case of carbon dioxide the blocking effect outweighs the moderate attraction of water for carbon dioxide, and in the case of hydrogen sulfide the higher attraction overcomes the blocking effect.

Acknowledgment

The authors gratefully acknowledge the assistance of Miss Claire Kaiser who made the majority of the permeability measurements reported here.

References

1. N. Riehl, Kolloid Zeitschrift No. 106, 201–206 (Mar. 1944).
2. S. A. Reitlinger, J. Gen. Chem. U.S.S.R. 14, 420–7 (1944).
3. M. Kleiber and F. R. Smith, Modern Packaging 18, No. 5, 117–118, 140 (Jan. 1945).
4. A. C. Schuman, Ind. Eng. Chem. Anal. Ed. 16, 58–60 (1944).
5. L. W. Elder, Modern Packaging 16, 69–71 (July 1943).
6. D. W. Davis, Modern Packaging 18, No. 9, 145 (May 1946).
7. V. L. Simril, and A. Hershberger, MODERN PLASTICS 27, 97, (June 1950).
8. Matheson Co., East Rutherford, N. J.
9. Simril, V. L., "The Sorption of Water Vapors by Polymers" Doctoral Thesis, Univ. of North Carolina, 1942.

VIII, the films are 1000 to 100,000 times as permeable to the vapors (benzene and ethanol) as to the gases (CO_2 and H_2S). Inasmuch as the vapor molecules are at least as large as the gas molecules, the gas permeability should be a reasonable measure of the maximum hole content available for either vapor or gas transmission. Therefore, almost all of the vapor permeability must result from the action of the vapor on the polymer. That this action should involve polymer intermolecular bond breaking and vapor solution seems quite reasonable. It is

Table VIII—Gas Versus Vapor Permeation

Film No. and type	Gas or Vapor	$P^* \times 10^9$ (at 25° C. for gases and 35° C. for vapors)
XVII Polythene	Benzene	286.5
	CO_2	0.274
XI Vinyl chloride/diethyl fumarate	Benzene	42.2
	CO_2	0.017
I Regenerated cellulose; no plasticizer	Ethanol	3.83
	H_2S	0.00005

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pyridine–N–oxide (EVPN) were prepared from the corresponding hydroxyethyl pyridines, and characterized. These N-oxides were polymerized with 2, 2′-azo-bis-isobutyronitrile. The monomer reactivity ratios of the following systems were determined: St/VPN ($r_1 = 0.11 \pm 0.01$; $r_2 = 2.1 \pm 0.6$), MMA/VPN ($r_1 = 0.13 \pm 0.03$; $r_2 = 3.9 \pm 0.8$), St/EVPN ($r_1 = 0.10 \pm 0.01$; $r_2 = 2.6 \pm 0.3$), and MMA/EVPN ($r_1 = 0.12 \pm 0.02$; $r_2 = 4.7 \pm 0.6$). Moreover the reactivity difference between vinylpyridine and vinylpyridine-N-oxide in copolymerization was discussed.

Aus dem Gummilaboratiorium der DEGUSSA Kalscheuren und dem
Physikalisch-Chemischen Laboratorium der DEGUSSA Konstanz

Kurzmitteilung

Kristallisationserscheinugen an gefüllten, nicht gedehnten Naturkautschukproben

Von H. Westlinning, G. Butenuth und G. Leineweber

(Eingegangen am 12. Oktober 1961)

〔30〕 高分子皮膜の気体，蒸気の透過性

第14報 吸湿高分子皮膜の気体透過性

伊 藤 行 雄*

要　旨　関係湿度を変えて，吸湿高分子皮膜の気体透過性を測定した。1) 分子鎖間に水素結合を多数有するポリビニルアルコールは，吸着水分の増大とともに透過係数(P)は著しく増大する。これは吸着された水分が膨潤を広くし，その結果，分子運動の活発化による試験侵度(D)の増大に基因する。2) 繊維素誘導体，ポリエチレンなどの場合には，低い関係湿度においては，吸着水分が気体の気散行程をふさぎ，その結果，Dは小さくなり，Pも小さくなる。しかし湿度が増すと，Pはポリビニルアルコールの場合と同様に増大する。

1. 緒　言

高分子皮膜のPに及ぼす湿度の影響については，すでに D.W. Davis[1]，V.L. Simril[2] らによって報告されている。しかし D, S（溶解度係数）についてはふれていない。よって著者はこの点について深く追究する必要を感じたので，ポリエチレン(PE)，繊維素誘導体，ポリビニルアルコール(PVA)などの気体透過性に及ぼす湿度の影響について研究を行なった。

2. 測定方法

水蒸気の透過係数(P_{H_2O})の測定は重量法，水蒸気以外の気体の透過の同時測定は圧力法により，測定方法などは，第5報[3]に報告したとおりである。関係湿度の調製方法は恒湿塩により，関係湿度は International critical table[4] によった。試料は24時間以上，測定湿度に接触させた後測定に供した。なお本測定方法では，蒸気が高分子皮膜に吸着したまま存在するのではないか…

Table 1 Humidity dependency on permeability of gasous through highpolymer films

Polymer	Gas	Temp. (°C)	RH	$P \times 10^4$ (cc·cm/ cm²·sec·cmHg)	$D \times 10^6$ (cm²/sec)	$S \times 10^2$ (cc/cm²·cmHg)
Polyvinylalcohol	CO_2	23	0	0.01		
	"	"	84	52		
	"	"	94	119	47.6	2.5
	N_2	14	0	<0.01		
	"	"	90	3.3	45.0	0.07
Cellophane	CO_2	14	0	0.01		
	"	"	95	10.5		
6 Nylon	"	30	0	1.0	1.8	0.55
	"	"	95	1.7		
	"	"	44	2.9	4.5	0.65
Polyethylene	"	15	0	61.4	175	0.35
($d=0.9203$)	"	"	43	57.8	155	0.37
	"	"	95	85.3	240	0.36
	N_2	"	0	4.5	180	0.025
	"	"	95	5.0		
	O_2	"	0	15.3	420	0.038
	"	"	43	15.3		
	"	"	95	18.8		
Polyvinylbutyral	CO_2	"	0	54.5	18.1	3.0
	"	"	95	31.0	6.2	—
Polyvinylchloride	"	20	0	4.2	1.8	2.4
	"	"	95	3.5		
Ethylcellulose	"	15	0	590		
	"	"	87	400		
Cellulose nitrate	"	20	0	29.7	9.0	3.3
	"	"	94	22.7	5.6	—
Cellulose acetate	"	"	0	52	26.0	2.0
	"	"	94	47	23.3	2.0
Cellulose acetate	"	"	0	36.5	16.3	2.2
(D.M.G.P 40 parts)	"	"	94	51.0	24.0	2.1

は便宜上の分類でしかなく，ポリエチレンの結果が示すように低温度において P_{gas} はわずか減少するが，高温度になると増加するように，2)，3) は温度，湿度の条件による差と考えられ，根本的な相違としては，1)に属するもの，2)3)に属するものの2大別できると考えられる。

3.1 酢酸繊維素 (AC)

前述の代表的なものとして酢酸繊維素(酢化度 53.1)についてみる。AC にジメチルグリコフタレート(DMGP)を種々な割合で添加したものの P_{CO_2} と関係湿度との関係を Fig. 1 に示した。可塑剤を含まない皮膜は関係湿度

Fig. 1 Permeability coefficient of cellulose acetate to carbondioxide as a function of relative humidities, 20℃

の増加とともに P_{CO_2} は低下するが，可塑剤含有皮膜は湿度の増加とともに P_{CO_2} は増加する。このことは一見奇異に感ずるが，前11報で可塑剤効果について報告したように，高分子-可塑剤系の P は可塑剤が少量の場合にはかえって減少し，可塑剤が増加すると P は増大する(AC の場合については Fig. 2 に示した)。皮膜に吸着された水分も可塑剤効果と同様の少量の場合には関膜充てん効果を与えるものと思われる。後述するように，繊維素親水性の水溶剤，炭酸ガス，窒素の拡散はほぼ同じ機構で行われるから，吸着された水分子は次に拡散してくる気体の通過をさえぎることになる。水分の S は空気体に比して非常に大きいから，水分はまず OH 基に結合するものと思われる。その部分の運動性は減ずる。その結果，気体の拡散は遅滞し，あるいは迂回するものと思われる。これらのことは透過の遅れ時間 (θ) から計算される D の温度結果 (Fig. 3) を見ても同様であり，P の減少は D に結因している。よってこの場合には可塑剤効果 W においても論じたよりも，さらに広い意味(湿潤現象も入れて)の C は拡散数 (φ_s) を考えなくてはならなく，D は(1)式で表されるものと思われる。

Film composition-parts plasticizer per 100 parts resin
○: dimethyl glycophthalate.
●: methylphthalyl-ethyleneglycolate

Fig. 2 Effect of plasticizers on the permeability coefficient of cellulose acetate to carbondioxide, 20℃

Fig. 3 Diffusion coefficient of cellulose acetate to carbondioxide as a function of relative humidities, 20℃

$$D = \frac{l^2}{6\theta} = D_0 \cdot \varphi_s \qquad (1)$$

しかるに OH 基が可塑剤で十分に溶媒和されている場合には，吸着される水分子は鎖間隙を大きくするのに役立ち，鎖の運動性を増し，その結果 D が増加し，P が増加する。この場合には湿度の増大と温度の上昇は同様な効果を与える。もちろん以上の結果から高分子単独皮膜において φ_s が温度が非常に大きくなれば，D, P は増加することが十分に想像できる。

3.2 ポリエチレン

結晶性高分子の湿度の影響についてポリエチレンの結果を Fig. 4 に示した。P_{CO_2} は関係湿度の増加に従って，小さな極小を経て増大する。P_{H_2O} については RH

左コラム

Fig. 4 Permeability coefficient of polyethylene to vapor (40°C) and carbondioxide (25°C) as a function of relative humidities

80% までは湿度依存性を有しないが，それ以上になると P_{H2O} は増加の傾向になる。ポリエチレンの $D_{H2O}=6.8 \times 10^{-8}$ cm²/sec で示されるように，窒素，炭酸ガスの D とほぼ同程度である。よって 3.1 酢酸繊維素で述べたと同様に非結晶領域に吸着された水分子は，気体の透過，拡散経路をふさぐことになる。このために拡散の遅滞，迂回が行なわれるものと思われる。ポリエチレンの場合には AC よりも気体の拡散が容易のために，吸着水はそれほど気体の拡散を妨害しないものと思われ，その結果 D の極小効果も小さい。結晶性高分子の気体，蒸気の拡散には (2) 式の φ を考えなくてはならないことを報告したが[1]，関係湿度の低いところでは吸着水分子によって起る新しい迂回効果の因子として φ_2 を考えれば説明できる。

$$D = \frac{l^2}{60} = D_0 \cdot \varphi \cdot \varphi_2 \qquad (2)$$

さらに湿度が増加すると吸着水分子は鎖の間隙を増大する方向に動き，1～2量体単位の回転運動が容易になり，気体，水蒸気の拡散はかえって容易になる。よって φ_2 は 1 に近づくとともに，D_2 自体も大きくなり，その結果 D_{gas} は増大し，P_{gas} は増加したものと思われる。P_{H2O} の濃度依存性の原因として，D_{H2O} が大きく影響しているものと思われる。もしDの影響とすると高湿度における P_{gas} の増大を説明できない。P_{H2O} に対する濃度依存性が低密度ポリエチレンより高密度ポリエチレンの方が大きいことは，結晶領域の近接部分が非結晶領域に比してかえって粗であるためと考えられ，そのような粗の部分をより多く有する高密度ポリエチレンの方が湿度依存性が大きくなるものと考えられる。

3.3 ポリビニルアルコール

セロハン・6 ナイロンについても湿度の与える影響は

中央コラム

PVA と同様であると考えられるので，PVA について詳しい検討を行なう。

3.3.1 皮膜の厚さ (l) と P の関係

第5報[1]で報告したように，圧力法で P を測定する場合には l が異なっても P はほとんど変らない。

3.3.2 P に及ぼす温度の影響

Figs. 5, Fig. 6 に P_{CO2}, P_{N2} に及ぼす関係湿度の影響を示した。P_{CO2}, P_{N2} は RH 45% まではわずかしか増加しないが，それ以上になると急激な増加を示す。平衡水分吸着量も同様にこの関係湿度から急激に増加することが知られている[1,10,18]。高湿度における P_{CO2}/P_{N2} は 15～20 の値を示す。この値は天然ゴム，ブタジエン，イ
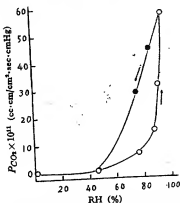
Fig. 5 Permeability coefficient of polyvinyl-alcohol to carbondioxide as a function of relative humidities, 15°C
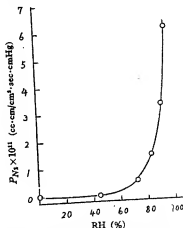
Fig. 6 Permeability coefficient of polyvinyl-alcohol to nitrogen as a function of relative humidities, 14°C

右コラム

ソイソブチレン，
イソブチレンの…
に温度の増加とと
履歴現象を示…
に報告されてい…
同一現象である…

3.3.3 θ に対…

関係湿度の増…
激に小さくなる…
ことが Fig. 7…

Fig. 7 T … alcohol … CO₂

しかし，…
しない。高…
ソブチレン…
OR 15 であ…
す。Fig. 8…
保湿度の影…
合致しない…
えられない…
による P の…

3.3.4

PVA は…
PVA の分…
よって水…
D_{H2O} も大…
合水とし…
-OH 基…
回転運動…
もなお，…
隣接の…
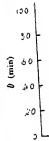
ァイソブチレンと同程度であり，また P_{gas} の値もポリイソブチレンのそれに近い。また Fig. 5 に示したように温度の増加と減少過程において，P は同じ点を通らず履歴現象を示す。これは武田[7]，著者[11]らによってすでに報告されている関係湿度−平衡水分張量との関係と同一現象であり，P_{gas} は関係湿度よりも炭酸水分量に影響されることを物語っている。

3.3.3 θ に及ぼす温度の影響

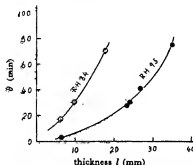関係湿度の増加に従って P が増大するとともに $θ$ は急激に小さくなる。高温度においては $θ$ は次式によく従うことが Fig. 7 の結果からわかる。

Fig. 7 Time lag for permeation (θ) of polyvinylalcohol as a function of the thickness (l), 23℃, CO₂.

$$D = \frac{l^2}{6θ} \qquad (3)$$

しかし，低温度においては，(3)式はそれほどよく合致しない。高温度において (3)式で計算された D はポリイソブチレンとほぼ等しい値を示し，かつ S は Hycar OR 15 のような極性を有する高分子とほぼ等しい値を示す。Fig. 8 に $1/θ$ (0.1 mm に内そうした値) に及ぼす関係湿度の影響を示した。低温度において (3)式はよく合致しないから，正確には $1/θ$ は P に比例すると は考えられないが，この図から少なくとも炭酸水分の増加による P の増大は D に起因すると考えてよい。

3.3.4 PVA の気体，水蒸気の拡散について

PVA の P_{gas}，D_{gas} の小さいことは，既述したようにPVA の分子間の水素結合の強力な点に基因している。よって水素結合の破壊の少ない低温度においては P_{H_2O}，D_{H_2O} も非常に小さい。PVA は側鎖として親水性の −OH 基を含む結晶性高分子であるから，吸着水はまず非結合として非結晶部分の −OH 基に結合すると考えられる。この場合には12 数の結晶で 1～2 量体の回転運動[11]はほとんど封固観と考えられ，その結果，P_{gas}，P_{H_2O} もまた小さい。さらに温度が増加すると吸着水は次々に鎖と鎖の間を結合している水素結合を破壊すると

考えられ，気体の拡散に対応する分子運動が徐々に可能になる。これ以上の吸着水は自由水となる結果，鎖と鎖の間に水分子が入りこんで分子間力を弱め，水分のない状態のガラス転移点以上と同様な分子運動が常温において起る。これは明らかに水の可塑化効果である。よって高温度下の気体，蒸気の P，D の急激な増加は，このような分子運動の活発化に起因していると思われる。PVAが 75℃ 前後においても，十分効果的な分子運動をもたないとして[11]，PVA の動的弾性率 (160℃) $E = 1 \times 10^9$ dyne/cm²，常温，高温度下における $E = 1 \times 10^8$ dyne/cm² から考えて[11]，常温，高温度下においては，拡散に対する十分効果的な分子運動が考えられる。PVA は常温においては小さな分子運動（側鎖の回転運動，鎖の小運動）も行なわれていないのに[11]，吸着水によって一挙にセグメント運動も可能になるためには P は急激に増加するしかるに鎖間に水素結合のような強力な結合を有しない高分子は，常温においても小さな分子運動はもちろんのこと，それ以上の大きな分子運動さえ行なわれている場合もある。そのような高分子（ポリエチレン，繊維素誘導体）は，多量の水の吸着により，前述のような分子運動が活発化されるにしかすぎないから，湿度の増加によっても P，D はわずかしか増加しない。PVA の場合には酢酸繊維素，ポリエチレンなどより著しく，温度の増加につれて P_{gas}，D_{gas} に極小効果が出ないのも上述の理由による。すなわち Fig. 9 に示したように P_{H_2O} は低温度下において，酢酸繊維素，ポリエチレン (Fig. 4) は温度依存性はなく，この濃度以下では S_{H_2O} は水蒸気圧上比例関係[9]，[10]にあると考えてさしつかえないから，D は水蒸気圧に影響されず，吸着水分量を 0 にそうして得られる D_{H_2O} の値は，酢酸繊維素 7.0×10^{-8} (25℃)，
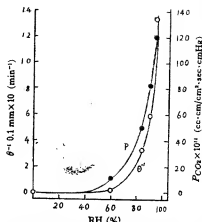

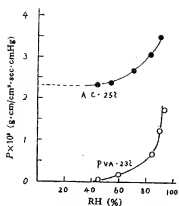Fig. 8 1/θ and permeability coefficient of polyvinylalcohol to carbondioxide as a function of relative humidities, 23℃

Fig. 9 Permeability coefficient of polyvinyl-
alcohol and cellulose acetate to water vapor
as a function of relaive humidities

ポリエチレン[1] $6.8×10^{-3}$ (20°C) cm[3] であり、窒素、
炭酸ガスの D とはほぼ同程度であるから、水分子の拡散
はこれらの気体の拡散と連携、迂回させるような効果を
与えるが、PVA の場合には D_{H_2O} は Fig. 9 から推定し
ても、また次献[14]からも $1×10^{-10}$ cm[3]/sec 程度である。
よってこのような場合には、水分子はもちろんのこと、
気体分子の拡散も容易ではない。さらに平衡水分吸着量
5% に減っても、$D_{H_2O}=1×10^{-9}$ cm[3]/sec[a] (20°C, RH
60%)であり、なお気体、水分子の拡散は不十分である。
しかるに濃度が増加すると分子運動が急激に活発になっ
て、水分子の拡散が十分に行なわれるようになる。
このときには拡散機構は十分活発であるから、もはや、
水分子、気体の両方の拡散が十分に行なわれ、P_{H_2O},
P_{gas} も急激に増大する。よって関係湿度の中間におい

でも P_{gas} に極小は表われない。よって前述した[6]傾向
に属するものは D_{H_2O} が非常に小さいものであり、2)
3) に属するものは水蒸気。気体の D は $1×10^{-6}$cm[3]/sec
程度の大きさを有するものであるといえる。なお高湿度
下の皮膜に含まれる自由水に対して、気体の溶解、拡散
も考えられるが、S については (20°C, 水の $S_{CO_2}=1.16$
$×10^{-3}$ cc/cm^{3}・cmHg)[14] 高分子の S とほとんど差がない
から問題にならない。自由水中の気体の拡散も存在する
とは考えられるが、筆者の測定範囲の温湿度下では、測定
された D の値から考えてそれほど大きな寄与はないと思
われ、P の増大は分子運動の活発化に基因する D の増大
が主因であるといえる。

文　　献

1) D.W. Davis : Paper Trade J., 29, 438 (1946)
2) V.L. Simril and A. Hershberger : Mod. Plast.,
   27, No. 11, 95(1950)
3) 伊藤行雄 : 高化, 17, 397 (1960)
4) National Research Councile : International critical
   Table, 1, 67 (1933) ; Mcgraw-hill Book Co., (N.Y.)
5) 伊藤行雄 : 工化, 64, 349 (1961)
6) 矢野 泰 : 工化, 59, 778 (1956)
7) 伊藤行雄 : 高化 投稿中
8) 小島賢次,安部明広 : 第9回高分子学会年次大会,
   濱 (1960. 6 大阪)
9) 武田文七 : 高化, 74, 128 (1953)
10) 伊藤行雄 : 高化, 17, 489 (1960)
11) 伊藤行雄 : 高化. 投稿中
12) 岡田紀夫, 慶 成煥 : 応用物理, 27, 104 (1958),
13) 野沢繁三 : 高化, 15, 105 (1958)
14) 日本化学会編 : 化学便覧, 596, 丸善 (1958).

Permeability of Gases and Vapors through High-polymer-films.

XIV. The Permeability of Gases through the Moistened
High-polymer-films

By Yukio Ito*

The permeability of gases through moistened highpolymer films has been measured at
various relative humidities. In the case of polyvinylalcohol the permeablity coefficient (P)
increase remarkably with the water content of films. Such increase of P may be attributed
to increase of diffusion coefficient due to activation of the segmental motions. On the
contrary, for cellulose derivatives and polyethylene, both P and D initially decrease and then
increase, passing through a minimum, with the increase of the relative humidity. The initial
reductions of P and D may be ascribed to the tortuous diffusion of the molecules of such
gases due to the distrebance by water molecules absorbed in the films.

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